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Principles and Practice

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AGRICULTURAL ANALYSIS

A Manual for the Study of Soils, Fertilizers, and Agricultural Products

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For the Use of Analysts, Teachers, and Students of Agricultural Chemistry

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SECOND EDITION, REVISED AND ENLARGED

VOLUME I.

SOILS

BY HARVEY W. WILEY, A.M., Ph.D.

EASTON, PA.
THE CHEMICAL PUBLISHING CO.
1906

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PREFACE TO VOLUME FIRST.

In this volume I have endeavored to place in the hands of teachers and students of Agricultural Analysis, and of analysts generally, the principles which underlie the science and art of the analysis of soils and the best approved methods of conducting it.

In the prosecution of the work I have drawn freely on the results of experience in all countries, but especially in the matter of the physical examinations of soils, of this country. Science is not delimited by geographic lines, but an author is not to be blamed in first considering favorably the work of the country in which he lives. It is only when he can see nothing of good outside of its own boundaries that he should be judged culpable. It has been my wish to give full credit to those from whose work the subject-matter of this volume has been largely taken. If, in any case, there has been neglect in this matter, it has not been due to any desire on my part to bear the honors which rightfully belong to another. With no wish to discriminate, where so many favors have been extended, especial acknowledgments should be made to Messrs. Hilgard, Osborne, Whitney, and Merrill, for assistance in reading the manuscript of chapters relating to the origin of soils, their physical properties, and mechanical analysis. With the wish that this volume may prove of benefit to the workers for whom it was written I offer it for their consideration.

H. W. WILEY.

Washington, D. C.,
Beginning of January, 1895.

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Preface to the Second Edition of Volume I.

So rapid has been the advance of agricultural science that in the preparation of the second edition of this volume it has been found necessary to practically rewrite it. A considerable part of the contents of the first edition of this volume relating as much, if not more, to fertilizers than to soils, has been transferred to the second volume, but new matter more than equivalent thereto in bulk has been inserted. The latest improved methods have been described, in so far as they are based on new principles or have secured better results. An attempt has been made to bring out more fully the principles of procedure involved in order that the present volume might not only mirror the latest advances in science, but also, to some extent, reflect the philosophy of method and practice. To this end, many of the older methods, long out of vogue, are retained, because in them are found the beginnings of fundamental procedures which serve to unify the processes of analysis and render more intelligible the modern methods.

The cordial reception accorded to the first edition of this manual encourages me to believe that the present volume will also be given a like welcome.

H. W. WILEY.

Washington, D. C.,
October 15, 1906.

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PART FIRST

INTRODUCTION

1. **Definitions.**—The term soil, in its broadest sense, is used to designate that portion of the surface of the earth which has resulted from the disintegration of rocks and the decay of plants and animals, and which is suited, under proper conditions of moisture and temperature, to the growth of plants. It consists, therefore, chiefly of mineral substances, together with some products of organic life, and of certain living organisms whose activity may influence vegetable growth either favorably or otherwise. The soil also holds varying quantities of gaseous matter and of water, which are important factors in its functions. The soil cannot be regarded as dead matter, but as a living organism exhibiting many most remarkable biological phenomena.

2. **Origin of Soil.**—Agriculturally considered, the soil proper is the older and more thoroughly disintegrated superficial layer of the earth, which has been longest exposed to weathering and the influences of organic life. It varies from a few inches to several feet in depth. The term subsoil is usually applied to a layer of soil beginning at the usual depth of cultivation and of a thickness of from six to nine inches. The surface of demarcation of change of color is sometimes regarded as the upper superficial boundary of the subsoil. The terms soil and subsoil are therefore not always used with the same relative signification. The subsoil is not as a rule so thoroughly disintegrated as the soil, since it is protected in a measure by the overlying material. It usually contains less organic matter than the soil. There is a freer circulation of air in the soil than in the subsoil, and the metallic elements usually exist in the upper layers as higher oxids. There is usually a notable difference in color between the soil and subsoil, and frequently a very sharp color line separates the two.

Geologically considered, the soil is that portion of the earth's

crust which has been more or less thoroughly disintegrated by weathering and other forces from the original rock formations, or from the sedimentary rocks, or from the unconsolidated sedimentary material. The soil has, therefore, the same essential constitution as the general mass of the earth, except that this débris has been subjected to the solvent action of water and the influence of organic life.

Preliminary to the proper understanding of the methods of the analysis of soils, there should be some definite knowledge concerning the composition of the earth's crust, so that the analyst may understand more thoroughly the origin and nature of the material he has to deal with, and thereby be better equipped for his work.

3. **The Chemical Elements Present in the Soil.**—The chemical elements present in the soil are naturally some or all of those which were present in the original rocks. For analytical purposes relating to agriculture, it is not necessary to take into account the rare elements which may occur in the soil, but only those need be considered which are present in some quantity and which enter as an important factor into plant growth or modify in some manner its physical properties. Of the whole number of chemical elements less than one-third are of any importance in soil analysis. These elements may be grouped into two classes, the non-metals, and the metals as follows:

Non-metals		Metals	
Oxygen,	Chlorin,	Aluminum,	Iron,
Silicon,	Phosphorus,	Calcium,	Manganese,
Carbon,	Nitrogen,	Magnesium,	Barium,
Sulfur,	Fluorin,	Potassium,	Titanium,
Hydrogen,	Boron.	Sodium,	Chromium.

4. **Atomic Weights.**—For the purpose of facilitating the calculation of results the latest revised table of atomic weights is given below.[1] All the known elements are included in this table for the convenience of analysts who may have to study some of the rarer elements in the course of their work.

[1] This table represents the latest and most trustworthy results reduced to a uniform basis of comparison with oxygen = 16 as starting point of the system.

TABLE OF ATOMIC WEIGHTS OF THE ELEMENTS[2]

Name.	Symbol.	Atomic weight.	Name.	Symbol.	Atomic weight.
Aluminum	Al	27.1	Neon	Ne	20.
Antimony	Sb	120.2	Nickel	Ni	58.7
Argon	A	39.9	Nitrogen	N	14.04
Arsenic	As	75.	Osmium	Os	191.
Barium	Ba	137.4	Oxygen	O	16.
Bismuth	Bi	208.5	Palladium	Pd	106.5
Boron	B	11.	Phosphorus	P	31.
Bromin	Br	79.96	Platinum	Pt	194.8
Cadmium	Cd	112.4	Potassium	K	39.15
Cesium	Cs	132.9	Praseodymium	Pr	140.5
Calcium	Ca	40.1	Radium	Ra	225.
Carbon	C	12.	Rhodium	Rh	103.
Cerium	Ce	140.25	Rubidium	Rb	85.5
Chlorin	Cl	35.45	Ruthenium	Ru	101.7
Chromium	Cr	52.1	Samarium	Sm	150.3
Cobalt	Co	59.	Scandium	Sc	44.1
Columbium	Cb	94.	Selenium	Se	79.2
Copper	Cu	63.6	Silicon	Si	28.4
Erbium	Er	166.	Silver	Ag	107.93
Fluorin	F	19.	Sodium	Na	23.05
Gadolinium	Gd	156.	Strontium	Sr	87.6
Gallium	Ga	70.	Sulfur	S	32.06
Germanium	Ge	72.5	Tantalum	Ta	183.
Glucinum	Gl	9.1	Tellurium	Te	127.6
Gold	Au	197.2	Terbium	Tb	160.
Helium	He	4.	Thallium	Tl	204.1
Hydrogen	H	1.008	Thorium	Th	232.5
Indium	In	115.	Thulium	Tm	171.
Iodin	I	126.97	Tin	Sn	119.
Iridium	Ir	193.	Titanium	Ti	48.1
Iron	Fe	55.9	Tungsten	W	184.
Krypton	Kr	81.8	Uranium	U	238.5
Lanthanum	La	138.9	Vanadium	V	51.2
Lead	Pb	206.9	Xenon	Xe	128.
Lithium	Li	7.03	Ytterbium	Yb	173.
Magnesium	Mg	24.36	Yttrium	Yt	89.
Manganese	Mn	55.	Zinc	Zn	65.4
Mercury	Hg	200.	Zirconium	Zr	90.6
Molybdenum	Mo	96.			
Neodymium	Nd	143.6			

PROPERTIES OF THE ELEMENTS.

Following is a brief description of the most important elements occurring in the earth's crust in respect of their relations to agriculture.

[2] Report of International Committee on Atomic Weights, Journal of the American Chemical Society, 1905, **27** : 1-7.

5. **Oxygen** exists in the free gaseous state in the atmosphere of which it constitutes about one-fifth by bulk, and in combination with other elements it forms nearly half the weight of the solid earth, and eight-ninths by weight of water. It enters into combination with most of the other elements, forming what are known as oxids, and with many of the elements it unites in several proportions, forming oxids of different composition. Combined with silicon, carbon, sulfur, and phosphorus, it forms an essential part of the silicates, carbonates, sulfates and phosphates, most of which are very abundant and all of which are very widely distributed in the earth's crust. In this form it is exceedingly stable and is rarely set free. With the exception of the oxids of silicon and iron these oxids seldom occur uncombined with the metals as constituents of rocks or soils. The oxids of iron very commonly occur as such in rocks and soils, and play a very important part in organic life. The several oxids of iron very frequently determine the color of soils; as the iron in a soil is more or less oxidized, or as it is exposed more or less to access of air, the color of the soil changes. These oxids of iron also play an important part in the absorptive capacities of soils for moisture and other physical conditions of soils, and also in the oxidation of organic matters in the soil. Many organic substances, and even the roots of growing plants when deprived of free access of air, can readily secure oxygen from the iron oxid, thus reducing the iron to a lower form of oxidation, the oxygen being used for the oxidation of the organic matter or for the needs of the growing plant; while the lower oxid of iron can easily take up the oxygen of the air and again be converted into a higher oxid ready again to give up a part of its oxygen and thus serve as a carrier.

6. **Silicon** never occurs in the free state, but combined with oxygen it forms silica, which constitutes free or in combination, more than one-half of the earth's crust. The oxid of silicon occurs in the very common form of quartz, and as silicate of alumina, lime or magnesia silicon forms an essential part of many minerals, such as the feldspars, amphiboles, pyroxenes and the micas, besides being an essential ingredient of many other minerals. Silica is relatively very slightly affected by the ordinary forces concerned in the decay of rocks, and even after the crystals of

feldspars, micas and other common minerals occurring in rocks have been disintegrated it remains as hard grains of sand, forming the bulk of most soils. By far the larger part of silicon in soils is in the form of grains of quartz more or less modified. This form of silica is probably chemically inert in regard to plant growth, but it plays a very important part in the physical structure of soils in its relations to plant nutrition.

7. **Carbon** as an elementary substance occurs as diamond and graphite and in an impure form as anthracite and bituminous coals. In peats and mucks carbon is the chief constituent. This substance is also contained in the organic matters of the soil known as humus, and the relation of the carbon to nitrogen often throws important light upon the amount and character of the nitrogenous matters. The humus content of the soil also affects its relation to water and to the absorption, retention and radiation of heat. In composition with oxygen it forms the chief food of growing plants, the carbon of the carbon dioxid of the air being elaborated into the tissue of the plants and the oxygen returned to the atmosphere. The content of carbon dioxid in the air is from three to five parts per 10,000 by volume. As a constituent of carbonates this element helps to form some of the most important ingredients of the earth's crust, namely, limestones, marbles, dolomites, etc., and as a result of organic activity it is found in the shells of the crustaceans. The calcareous matters of the soil, that is, the carbonates of lime therein found, are of the highest importance from an agricultural point of view. They not only favor the process of converting nitrogenous bodies into forms suitable for plant food, but also exert a most potent influence on the physical state of the soil and its capacity for holding water and permitting its flow to the rootlets of the plant.

8. **Sulfur** occurs in nature in both the free and combined state. In the free state it is found in volcanic regions such as Sicily, Iceland, and the western United States. Its usual form of occurrence is in combination with the metals to form sulfids, or with oxygen and a metal to form sulfates. Sulfur and iron combine to form iron pyrites or iron disulfid (FeS_2), while sulfur, oxygen, and calcium are found in gypsum, an important fertilizing compound.

Sulfur plays an important part in the nourishment of plants, being found in them both as sulfuric acid and in organic compounds; it is an essential constituent of both animal and vegetable protein and is thus intimately associated with one of the most important classes of foods.

9. **Hydrogen** is a colorless, invisible gas, without taste or smell. It occurs free in small proportions in certain volcanic gases, and in natural gas, but its most common form is in combination with oxygen as water (H_2O), of which it forms 11.19 per cent. by weight. It also occurs in combination with carbon to form the hydrocarbons, such as the mineral oils (petroleum, etc.) and gases. Hydrogen is of no importance to agriculture in a free state, but water is the most important and necessary of all plant foods.

10. **Chlorin** occurs free in nature only in limited amounts in volcanic vents. Its most common form is in combination with hydrogen, forming hydrochloric acid, or with the metals to form chlorids. It combines with sodium to form sodium chlorid or common salt (NaCl), which is the most abundant mineral ingredient in sea water and which can usually be detected in rain and ordinary terrestrial waters. In this form, also, it exists as extensive beds of rock salt, which is mined for commercial purposes.

Chlorin is found uniformly in plants and may be regarded as a common constituent thereof. Common salt applied to a soil modifies its power of attracting and holding water but it cannot be said to have any marked fertilizing value. In excess it proves highly injurious and even fatal to vegetation.

11. **Phosphorus** never occurs in nature in a free state but exists in combination in greater or less quantities in all soils and in many minerals. Its combinations are also found in large deposits of mineral known as phosphorite and apatite and as so-called pebble deposit and phosphate rock. Phosphorus in some sort of combination is one of the most essential elements in animal and plant food. In animals its compounds form almost all of the mineral matter of the bones, and in plants they are important constituents of the ash of seeds. It exists in organic combination both in animal and vegetable tissues such as lecithines and other compounds.

The mineral deposits of phosphorus, as well as bones, are chiefly tri-calcium phosphate, while the slag compound resulting from the basic treatment of iron ores rich in phosphorus is a tetra-calcium salt.

The pebble deposits and some rock phosphates are supposed to be of organic origin, derived from the remains of marine, terrestrial and aerial animals. The mean content of phosphorus found in 211 samples of volcanic and crystalline rocks is 0.22 per cent.[3]

12. **Nitrogen** as a mineral constituent of soils, is found chiefly in the form of nitrates, but, owing to their solubility, they can not accumulate in soils exposed to heavy rainfalls. The gaseous nitrogen in the soil is also of some importance, since it is on this material that the organisms which have a symbiotic activity with the rootlets of some plants probably act in the process of the fixation of atmospheric nitrogen in a form accessible to plants. Nitrogen in the free state, it is believed, is not directly absorbed into the tissues of green plants. It is necessary that it be oxidized in some way to nitric acid or some compound containing it before it can be assimilated. The importance of nitrogen as a plant food can not be too highly estimated. It is as necessary to plant growth and development as water, phosphoric acid, lime and potash, and is far more costly. While a large quantity of nitrogen exists in the air in an uncombined state, it is, nevertheless, one of the least abundant of the available elements of high importance in plant nutrition.

The conservation and increase of the stores of available nitrogen in the soil is one of the chief problems occupying the attention of agricultural chemistry. Nitrogen, which is not immediately available for the growth of plants, is conserved and restored by natural processes in various ways. A further discussion of this subject is found in the second volume of this work.

13. **Boron** occurs chiefly in volcanic regions, but is much more widely distributed in the soil than formerly believed. It is a constituent of the ash of many plants, and is thought by some to be a true plant food.[4] A more reasonable theory is that its presence in vegetable products is a mere incident to its occur-

[3] Bulletin Philosophical Society of Washington, 11 : 136.

[4] Crampton : American Chemical Journal, 1890, 2 : 227.

rence in the soil. It is one of the least abundant of the elements, not occurring in sufficient quantity to find a place in the table showing their relative abundance, which is to follow. Boric acid and borax are used to some extent as a preservative, especially in meats and dairy products.

14. **Fluorin** does not occur free in nature, but it exists chiefly in combination with calcium, forming fluorspar, traces of which are found widely distributed. In combination chiefly with lime it occurs in bone, teeth, blood, and the milk of mammals. It is one of the elements which does not combine with oxygen, and it can be isolated only with the greatest difficulty. At most only very small traces of it are found in soils. Fluorid of lime is found, however, in considerable quantities in certain phosphate deposits.

15. **Aluminum** is, probably, next to oxygen and silicon, the most abundant element of the earth's crust, of which it is estimated to form about one-twelfth. It has never been found, in nature, in the free state, but commonly occurs in combination with silicon and oxygen, in which form it is an abundant constituent of feldspar, mica, kaolin, clay, slate, and many other rocks and minerals.

By the weathering of feldspar, mica, and other minerals containing aluminum, true clay is formed, which is of the greatest importance in the constitution of the soil. The compounds of aluminum are not important as plant food except when they contain potash but they form valuable constituents of the soil, furnishing a large part of its bulk, and modifying in the most profound degree its physical properties. It is the custom of some authors to use the word clay to designate the fine particles of soil which have in general the same relations to moisture and tilth as the particles of weathered feldspar, etc. In a strict chemical sense, however, the term clay is applied only to the silicates of alumina and the silica found therewith formed as indicated above. The fertility of a soil is indirectly dependent on the quantity of clay which it contains, its relations to moisture and amenability to culture being largely conditioned by its clay content. The determination of the percentage of clay in soils is an operation of the highest

utility in forming an opinion of the value of a soil based on physical data alone.

16. **Calcium** is one of the commonest and most important elements of the earth's crust, of which it has been estimated to compose about one-sixteenth. It does not occur free in nature, but its most common condition is in combination with carbon dioxid, forming the mineral calcite, and as marble, and the very abundant limestone rocks. In this form it is slightly soluble in water, especially when containing carbon dioxid, and hence lime is very generally found in natural waters, in which it furnishes the chief ingredient necessary for the formation of the shells and skeletons of the various species of mollusca and corals. In combination with sulfuric acid calcium forms the rock gypsum. Lime is not only a necessary plant food, but also influences in a marked degree the physical condition of the soil and the progress of nitrification. Many stiff clay soils are rendered porous and pulverulent by an application of lime, and thus made far more productive. The sourness or acidity of soils is also corrected by the application of lime. Although existing in great abundance it has not commanded the degree of attention from farmers and agricultural chemists which its merits deserve. It forms an essential ingredient of plants and animals, in the latter being collected chiefly in the bones, while in plants it is rather uniformly distributed throughout all the tissues. Both in common language and in chemistry the term lime is applied to the product of burning limestone (carbonate of lime) until the carbon dioxid is expelled. In the freshly burned state lime contains no water. When exposed to the air it gradually absorbs water in chemical combination and becomes slaked lime. This change takes place with great rapidity and with the evolution of much heat on the application of water.

17. **Magnesium** occurs chiefly in combination with silica and carbon dioxid or with lime and carbon dioxid in the mineral dolomite. It is intimately associated with calcium and a trace of it is nearly always found where lime occurs in any considerable quantity. The bitter taste of sea water and some mineral waters is often due to the presence of salts of magnesia. In combination with silica it forms an essential part of such rocks as serpentine,

soapstone, and talc. Magnesia is useful, especially in the formation of seeds, but it is not absent from other parts of the plant. It performs its functions best in the presence of calcium compounds and in the absence of the latter magnesia salts may easily be injurious.

18. **Potassium** combined with silica is an important element in many silicates as, for instance, orthoclase. Granite rocks usually contain considerable quantities of potassium, and on their decomposition this becomes available for plant food. In the form of chlorid, potassium is found in small quantities in sea water, and as a nitrate it forms the valuable salt known as niter or saltpeter. Potassium, as is the case with phosphorus, is universally distributed in soils, and forms one of the great essential elements of plant food. Under the form of kainite and other minerals large quantities of potassium are used for fertilizing and for the manufacture of pure salts for commercial and pharmaceutical purposes. The ordinary potassium salts are very soluble and for this reason they can not accumulate in large quantities in soils exposed to heavy rainfall. In the form of carbonate, potassium forms one of the chief ingredients of hard wood ashes, and in this form of combination is especially valuable for fertilizing purposes. Potash salts, being extremely soluble, are likely to be held long in solution. Some of them are recovered in animal and vegetable life, but the great mass of potash carried into the sea still remains unaccounted for. The recovery of the waste of potash is chiefly secured by the isolation of sea waters containing large quantities of this salt and their subsequent evaporation. Such isolation of sea waters takes place by means of geological changes in the level of the land and sea. In the raising of an area above the water level there is almost certain to be an enclosure, of greater or less extent, of the sea water in the form of a lake. This enclosure may be complete or only partial, the enclosed water area being still in communication with the main body of the sea by means of small estuaries. If this body of water be exposed to rapid evaporation as was doubtless the case in past geological ages, there will be a continual influx of additional sea water through these estuaries to take the place of that evaporated. The waters may thus become more and more charged with saline constituents. Finally a point

is reached in the evaporation when the less soluble of the saline constituents begin to be deposited. In this way the various formations of mineral deposits, produced by the drying up of enclosed waters takes place. The principles of physical chemistry explain the manner in which these saline deposits are laid down.[5] An account of the deposition of the potash salts near Stassfurt, Germany, is found in Vol. II.

19. **Sodium** is never found free in nature, but its most common form is in combination with chlorin as common salt, an important ingredient of sea water. Combined with silica sodium is an important element in many silicates. Sodium, although closely related to potassium chemically, cannot in any case be substituted therefor in plant nutrition. While it is certain that plants can thrive without a trace of sodium, it is believed to be helpful in some cases, and its salts may replace those of potassium in so far as osmotic and neutralizing functions are concerned. In combination with nitrogen it forms soda (or Chile) saltpeter which is a valuable fertilizer on account of its content of nitric acid.

20. **Iron** is the most abundant of the heavy metals, and occurs in nature both free and combined with other elements. In the free state it is found only to a limited extent in basaltic rocks and meteorites, but in combination with oxygen it is one of the most widely diffused of metals, and forms the coloring matter of a large number of rocks and minerals. In this form, too, it exists as the valuable ores of iron known as magnetite and hematite. In combination with sulfur it forms the mineral pyrite, FeS_2. The yellow and red colors of soils are due chiefly to iron oxids. Iron salts are essential to the production of chlorophyll, and to its functional activity. Iron is one of the essential constituents of the haemoglobin of the blood without which oxygen could not be properly carried to every part of the body.

21. **Titanium** is apparently of no importance in plant nutrition, but its occurrence in many soils requires recognition in soil analysis. It has been found to be one of the most widely distributed elements.[6]

[5] Van't Hoff (Chicago University lectures).

[6] Dunnigton: Proceedings of the American Association for the Advancement of Science, **84** : 132; American Journal of Science, **42** : 491; American Chemical Journal, **10** : 36; Baskerville: Journal American Chemical Society, **21** : 1099.

22. **Manganese,** next to iron, is the most abundant of the heavy metals. It occurs in nature in combination with oxygen, in which form it is associated in minute quantities with iron in igneous rocks or in the forms known mineralogically as pyrolusite, psilomelane and wad. As the peroxid of manganese it occurs in concretionary forms scattered abundantly over the bottom of the deep sea. It is found in the ash of some plants, but is not believed to be an essential to plant growth.

23. **Chromium** in so far as known takes no part in plant nutrition and its occurrence in the soil is only of importance from an analytical and color standpoint.

24. **Barium** occurs in nature combined with sulfuric acid, forming the mineral barite, or heavy spar, or with carbon dioxid forming the mineral witherite. It is of small importance from an agricultural standpoint.

25. **Relative Abundance of the More Important Chemical Elements.**—It will be of interest to the agricultural analyst to know as nearly as possible the relative abundance of the more important chemical elements. This subject has been carefully studied by Clarke on data supplied by Woodward.[1] The materials considered in these calculations are the atmosphere, the water, and the solid crust of the earth to the depth of 10 miles below the sea level. Of these materials, assuming the mean density of the earth's crust to the depth of 10 miles to be 2.5, the relative quantities of the three constituents named are as follows:

	Per cent.
Atmosphere	0.03
Water	7.08
Solid crust of the earth to a depth of 10 miles	92.89

According to these calculations the relative abundance of the important elements composing the atmosphere, the water of the ocean and the solid crust of the earth to the depth given is as follows:

[1] Bulletin of the Philosophical Society of Washington, 2 : 131 et seq.

	Solid crust, 93 per cent.	Ocean, seven per cent.	Mean, including air.
Oxygen	47.29 per cent.	85.79 per cent.	49.98 per cent.
Silicon	27.21 " "	.... " "	25.30 " "
Aluminum	7.81 " "	... " "	7.26 " "
Iron	5.46 " "	.... " "	5.08 " "
Calcium	3.77 " "	0.05 " "	3.51 " "
Magnesium	2.68 " "	0.14 " "	2.50 " "
Sodium	2.36 " "	1.14 " "	2.28 " "
Potassium	2.40 " "	0.04 " "	2.23 " "
Hydrogen	0.21 " "	10.67 " "	0.94 " "
Titanium	0.33 " "	.... " "	0.30 " "
Carbon	0.22 " "	0.002 " "	0.21 " "
Chlorin	0.01 " "	2.07 " "	0.15 " "
Bromin	.... " "	0.008 " "	
Phosphorus	0.10 " "	.... " "	0.09 " "
Manganese	0.08 " "	.... " "	0.07 " "
Sulfur	0.03+ "	0.09 " "	0.04+ "
Barium	0.03 " "	.... " "	0.03 " "
Nitrogen	.... " "	.... " "	0.02 " "
Chromium	0.01 " "	.... " "	0.01 " "
	100.00 " "	100.000 " "	100.00 " "

Nineteen of the more important elements are included in the above table. The aggregate of all the other elements can not be more than one per cent. of the earth's crust, and is probably less than that amount, and no one of them could exceed five-tenths per cent. Most of them occur in such minute quantities as to render any attempt to express them numerically futile.

26. **Fluorin** is not mentioned in this table but it is stated that its probable percentage is two-tenths to three-tenths making it thus slightly more abundant than nitrogen.

One of the points of interest in connection with this table is that nitrogen which is regarded by most persons as one of the most abundant of the elements is almost the least abundant of those mentioned.

THE MINERALS OCCURRING IN ROCKS.

27. **The Soil,** as before stated, being composed almost exclusively of decayed rocks, its characteristics would naturally be determined in great part by the character of the minerals contained in the rocks.

A rock may be composed of a single mineral or an aggregation of several minerals.

According to Merrill, rocks may occur either in the form of stratified beds, eruptive masses, sheets or dikes, or as veins and other chemical deposits of comparatively little importance as regards size and extent.[8] The mineral composition of rocks is greatly simplified by the wide range of conditions under which the commonest minerals can be formed. Thus quartz, feldspar, mica, and the minerals of the hornblende, or pyroxene group, can be formed from a mass cooling from a state of fusion; they may be crystallized from solution, or be formed from volatilized products. They are therefore the commonest of minerals and are rarely absent in rocks of any class, since there is no process of rock formation from which they are necessarily excluded.

Most of the common minerals, like the feldspars, micas, hornblendes, pyroxenes, and the alkaline carbonates possess the capacity of adapting themselves to a very considerable range of compositions. In the feldspars, for example, lime, soda, or potash may replace one another almost indefinitely, and it is now commonly assumed that true species do not exist, but all are but isomorphous admixtures passing into one another by all gradations, and the names albite, oligoclase, anorthite, etc., are to be used only as indicating convenient stopping and starting points in the series. Hornblende or pyroxene, further, may be pure silicate of lime and magnesia, or iron and manganese may partially replace these substances. Lime carbonate may be pure, or magnesia may replace the lime in many proportions.

These illustrations are sufficient to show the reason for the great simplicity of rock masses as regards their chief mineral constituents.

Whatever may be the conditions of the origin of a rock mass, the probabilities are that it will be formed essentially of one or more of a half a dozen minerals in some of their varieties.

But however great the adaptability of these few minerals may be they are, nevertheless, subject to very definite laws of chemical equivalence. There are elements which they cannot take into their composition, and there are circumstances which retard their

[8] Handbook Department of Geology, U. S. National Museum, 508, et seq.

formation while other minerals may be crystallizing. In a mass of rock of more or less accidental composition formed under these widely varying conditions it may, therefore, be expected that other minerals will form, in considerable numbers, but minute quantities. It is customary to speak of those minerals which form the chief ingredients of any rock, and which may be regarded as characteristic of any particular variety, as the essential constituents, while those which occur in but small quantities, and whose presence or absence does not fundamentally affect its character, are called accessory constituents. The accessory mineral which predominates, and which is, as a rule, present in such quantities as to be recognizable by the unaided eye, is the characterizing accessory. Thus a biotite granite is a stone composed of the essential minerals quartz and potash feldspar, but in which the accessory mineral biotite occurs in such quantities as to give a definite character to the rock.

28. Classification of Minerals.—The minerals of rocks may also be conveniently divided into two groups, according as they are products of the first consolidation of the mass or of subsequent changes. This is the system here adopted. We thus have:

(1) The original or primary constituents, those which formed upon the first consolidation. All the essential constituents are original, but on the other hand all the original constituents are not essential. Thus, in granite, quartz and orthoclase are both original and essential, while beryl, zircon or apatite, though original, are not essential.

(2) The secondary constituents are those which result from changes in a rock subsequent to its first consolidation, changes which are due in great part to the chemical action of percolating water. Such are the calcite, chalcedony, quartz, and zeolite deposits which form in the druses and amygdaloidal cavities of traps and other rocks.

Below is given a list of the more common, original and secondary minerals occurring in rocks. It will be observed that the same mineral may, in certain cases, occur in both original and secondary forms. The tables following of original and secondary minerals are given by Merrill.[9]

[9] Rocks and Soils, 11–12; Handbook for Department of Geology, 510.

A. Original Minerals

1. Quartz.
2. The Feldspars.
   - 2a. Orthoclase.
   - 2b. Microcline.
   - 2c. Albite.
   - 2d. Oligoclase.
   - 2e. Andesite.
   - 2f. Labradorite.
   - 2g. Bytownite.
   - 2h. Anorthite.
3. The Amphiboles.
   - 3a. Hornblende.
   - 3b. Tremolite.
   - 3c. Actinolite.
   - 3d. Arvedsonite.
   - 3e. Glaucophane.
   - 3f. Smaragdite.
4. The Monoclinic Pyroxenes.
   - 4a. Malacolite.
   - 4b. Diallage.
   - 4c. Augite.
   - 4d. Acmite.
   - 4e. Aegerite.
5. The Rhombic Pyroxenes.
   - 5a. Enstatite (Bronzite).
   - 5b. Hypersthene.
6. The Micas.
   - 6a. Muscovite.
   - 6b. Biotite.
   - 6c. Phlogopite.
7. Calcite (and Aragonite).
8. Dolomite.
9. Gypsum.
10. Olivine.
11. Garnet.
12. Epidote.
13. Zoisite.
14. Andalusite
15. Staurolite.
16. Scapolite.
17. Elæolite and Nepheline.
18. Leucite.
19. Sodalite.
20. Hauyn (nosean).
21. Apatite.
22. Menaccanite.
23. Magnetite.
24. Hematite.
25. Chromite.
26. Halite (common salt).
27. Fluorite.
28. Graphite.
29. Carbon.
30. Pyrite.

B. Secondary Minerals

1. Quartz.
   - 1a. Chalcedony.
   - 1b. Opal.
   - 1c. Tridymite.
2. Albite.
3. The Amphiboles.
   - 3a. Hornblende.
   - 3b. Tremolite.
   - 3c. Actinolite.
   - 3d. Uralite.
4. Muscovite (Sericite).
5. The Chlorites.
   - 5a. Jefferisite.
   - 5b. Ripidolite.
   - 5c. Penninite.
   - 5d. Prochlorite.
6. Calcite (and Aragonite).
7. Wollastonite.
8. Scapolite.
9. Garnet.
10. Epidote.
11. Zoisite.
12. Serpentine.
13. Talc.
14. Glauconite.
15. Kaolin.
16. The Zeolites.
    - 16a. Pectolite.
    - 16b. Laumontite.
    - 16c. Phrenite.
    - 16d. Thomsonite.
    - 16e. Natrolite.
    - 16f. Analcite.
    - 16g. Datolite.
    - 16h. Chabazite.
    - 16i. Stilbite.
    - 16k. Heulandite.
    - 16l. Phillipsite.
    - 16m. Ptilolite.
    - 16n. Mordenite.
    - 16o. Harmotome.
17. Hematite.
18. Limonite.
19. Göthite.
20. Turgite.
21. Pyrite.
22. Marcasite.

Of the above named minerals the feldspars, zeolites, calcite and kaolin are of particular interest to agriculture.

ROCKS AND ROCK DECAY.

29. Types of Rocks.—Rocks may be divided in reference to their structure into four types:[10] First, crystalline; second, vitreous; third, colloidal; fourth, fragmental.

Of these classes there may be selected, as types of the first order, granite and crystalline limestone.

The second class is typically represented by obsidian. Rocks of this kind are confined to a volcanic origin.

The third class of rocks is completely amorphous in its structure and is less common than the others. It is found only in rocks of chemical origin. Types of this class are the siliceous sinters, opals, flint nodules, and many serpentines.

Of the fourth class of rocks, sandstone is typical, being comprised wholly of fragments of rocks pre-existing. The particles may be held together either by cohesion or by a cement composed of silica, iron oxids, carbonate of lime or clayey matter.

30. The Microscopical Structure of Rocks.—A great deal more light is thrown upon the nature of rock materials by microscopical study than by their study in bulk. The requisites for a microscopical study of rock are that the material should be cut into extremely thin laminae with parallel sides and polished so as to transmit the light freely. The study of the crystalline structure of the material is then conducted by means of a microscope furnished with polarizing and analyzing appliances. The light before passing through the mineral film may be polarized by a Nicol prism. After passing through the film it is analyzed by a second Nicol prism. In this way the crystalline structure of the rock as affecting polarized light is distinctly brought out. The thickness of the films examined should be from $^1/_{500}$ to $^1/_{600}$ of an inch.

The method of rock study by thin microscopic sections is one of comparatively recent origin.

The value of the method is based upon the fact that every crystalline mineral has certain definite optical properties. Therefore, when a crystalline mineral is distorted or misshapen so as to be

[10] Merrill: Handbook of Geology, 512.

incapable of identification by the ordinary method, it can be at once identified by its optical examination in the manner just described. In this way not only can one mineral be distinguished from another, but the crystalline system to which it belongs can be accurately pointed out. The value of the method is well summed up by Merrill, who says that it is not merely an aid in determining the mineralogical composition of a rock, but also, which is often much more important, its structure and the various changes which have taken place in it since its first consolidation.[11] Rocks are not the definite and unchangeable mineral compounds they were once considered, but are rather ever varying aggregates of minerals which even in themselves undergo structural and chemical changes almost without number.

Another valuable result of such a study is illustrated by the discovery that the structural features of a rock are not dependent alone upon its chemical composition or geological age, but also upon the conditions under which it cooled from the molten magma. Portions of the same rock may vary all the way from a wholly crystalline to a purely vitreous form.

In the road material laboratory of the Bureau of Chemistry the study of microscopic structure of the substances used for surfacing roads leads to results of the highest practical importance.

Some typical microstructures of crystalline rocks are shown in the accompanying plates I-III.[12]

Although this method of study has thus far been confined mainly to crystalline rocks, its efficiency is by no means limited to them. The fragmental rocks and their decomposed débris to which the name soil is given are equally worthy of study by this method. Indeed, the full value of a chemical analysis of any rock or soil can not be ascertained unless such an analysis is accompanied by a microscopic examination. It is desirable to know not merely what there is in any soil, but in what physical form these compounds exist. To this latter question the chemical analysis as ordinarily made will give no clew. An outline of the method of analysis is given in the proper place.

[11] Handbook for Department of Geology, 515.

[12] Bulletin No. 79 Bureau of Chemistry, Plates I–IV.

Fig. 1.—Basalt (Trap).

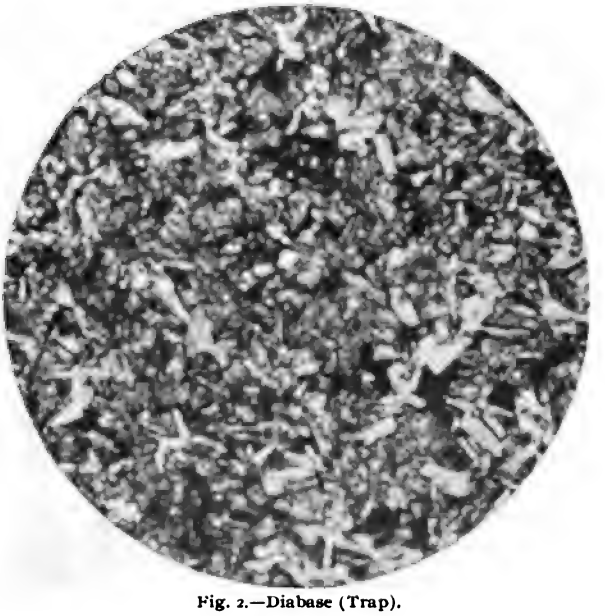


Fig. 2.—Diabase (Trap).

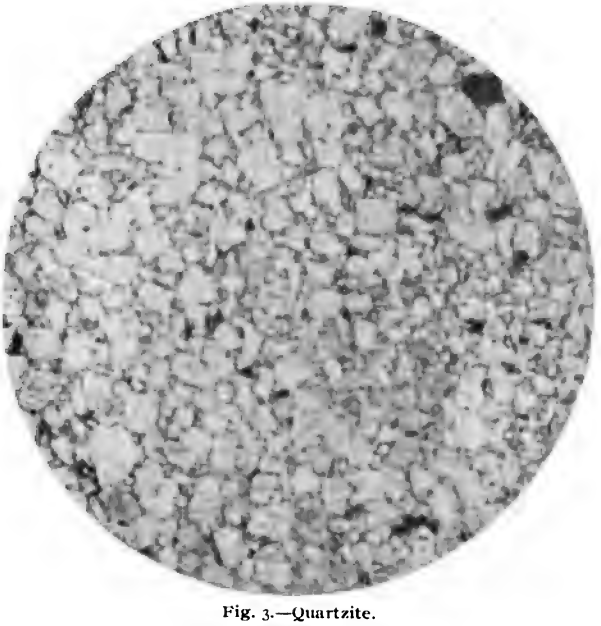


Fig. 3.—Quartzite.

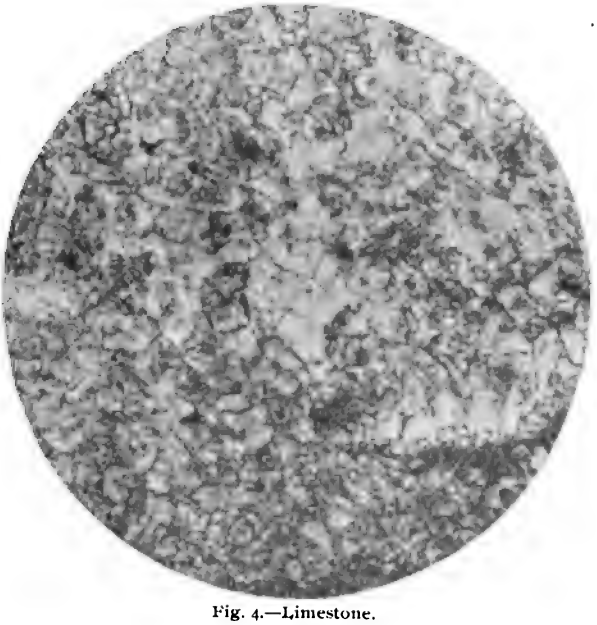


Fig. 4.—Limestone.

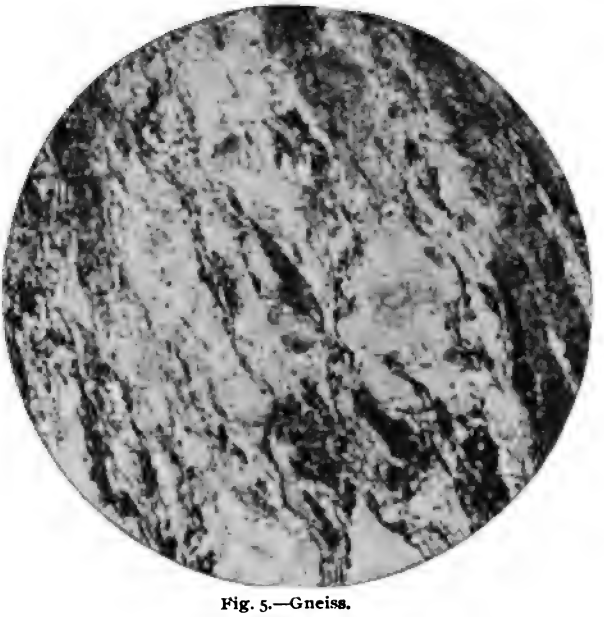


Fig. 5.—Gneiss.

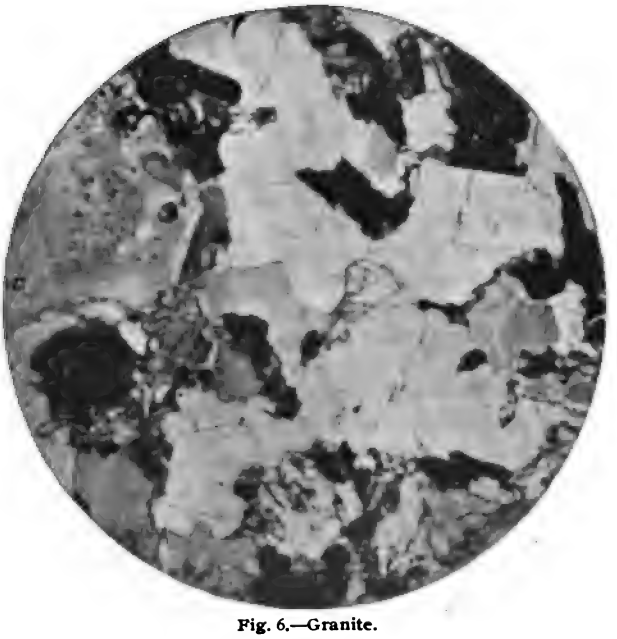


Fig. 6.—Granite.

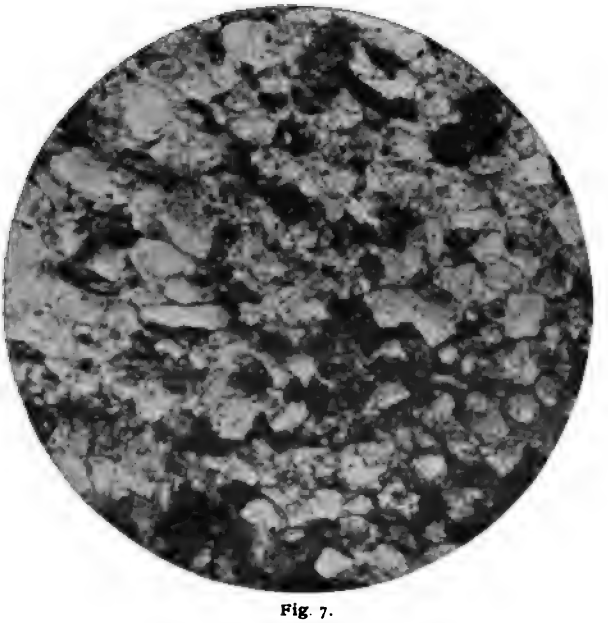


Fig. 7.
Microscopic Structure of Sandstone.

31. **Specific Gravity.**—Much information in regard to the properties of a rock, or mineral constituent thereof, may be derived from its specific gravity.

The internal structure of a rock may have much to do with its apparent specific gravity. As an instance of this, it may be stated that an obsidian pumice will float upon water, buoyed up by the air contained in its vesicles, while a compact obsidian of the same composition will sink immediately. A careful discrimination must, therefore, be made between apparent and true specific gravity. In general it may be said that crystalline rocks have a higher specific gravity than those of a vitreous nature. The specific gravity is, therefore, largely dependent upon chemical and crystallographic properties; for instance, among siliceous rocks those which contain the largest amount of silica are the lightest, while those with a comparatively small amount, but rich in iron, lime, magnesia and baryta are heaviest.

32. **Chemical Classification of Rocks.**—Rocks are often classified in respect of the chief mineral constituent which they contain. Rocks which are composed largely of lime are termed calcareous; of silica, siliceous; of iron, ferruginous and of clay, argillaceous. In respect of eruptive rocks, it is customary to speak of those which show above 60 per cent. of silica as acidic, while those containing less than 50 per cent. of silica and a correspondingly larger amount of iron, lime, and magnesia, are spoken of as basic. Illustrations of the classification of rocks on the above principles are given below.[18]

STRATIFIED ROCKS

Kind.	Specific gravity.	Composition
Calcareous:		
Compact limestone	2.6 to 2.8	Carbonate of lime.
Crystalline limestone		
Compact dolomite	2.8 to 2.95	Carbonate of lime and magnesia.
Crystalline dolomite		
Siliceous:		
Gneiss	2.6 to 2.7	Same as granite.
Siliceous sandstone	2.6	Mainly silica.
Schist	2.6 to 2.8	60 to 80 per cent. silica.
Argillaceous:		
Clay slate (argillite)	2.5	Mainly silicate of alumina.

[18] Merrill: Handbook of Geology, 521; Rocks and Soils, 45.

ERUPTIVE ROCKS

	Specific gravity.	Per cent. silica.
Acidic Group:		
Granite	2.58 to 2.73	77.65 to 62.90
Liparite	2.53 to 2.70	76.06 to 67.61
Obsidian	2.26 to 2.41	82.80 to 71.19
Obsidian pumice	Floats on water	82.80 to 71.19
Intermediate Group:		
Syenite	2.73 to 2.86	72.20 to 54.65
Trachyte	2.70 to 2.80	64.00 to 60.00
Hyalotrachyte	2.4 to 2.5	64.00 to 60.00
Andesite	2.54 to 2.79	66.75 to 54.73
Basic Group:		
Diabase	2.66 to 2.88	50.00 to 48.00
Basalt	2.90 to 3.10	50.59 to 40.74
Peridotite	3.22 to 3.29	42.65 to 33.73
Peridotite (iron rich)	3.86	23.00
Peridotite (meteorite)	3.51	37.70

33. **Color of Rocks.**—The color of rocks is determined chiefly by the oxids of metals which they contain and the degree of oxidation of the mineral in each particular case. There are, however, many colors of rocks which seem to depend not upon any particular mineral ingredient, but upon some particular crystalline structure or physical condition.[14]

The chief coloring matters in minerals are those which form colored bases such as iron, manganese, chromium, etc. The yellow, brown, and red colors, common to fragmental rocks, are due almost wholly to free oxids of iron. The gray, green, dull brown, and even black colors of crystalline rocks are due to the presence of free iron oxids or to the prevalence of silicate mineral rich in iron, as augite, hornblende, or black mica. Rarely copper and other metallic oxids than those of iron are present in sufficient abundance to impart their characteristic hues. As a rule, a white or light-gray color denotes an absence of an appreciable amount of iron in any of its forms. The bluish and black colors of many rocks, particularly the limestones and shales, are due to the presence of organic matter.

In still other cases, and particularly the feldspar-bearing rocks, the color may be due to the physical condition of the feldspar.

[14] Merrill: Smithsonian Report, 1890; Handbook of Geology, 521.

Inasmuch as the color of rocks is due so largely to metallic oxids, it is easy to see that they may undergo changes when exposed to weathering, or the degree of oxidation may change, and either, together with changes in the physical structure of the rock, may cause a distinct change in color. Luster is often considered in connection with color, and is due almost exclusively to physical conditions.

34. **Kinds of Rocks.**—The rocks which form any essential part of the earth's crust are grouped under four main heads, the distinction being based upon their origin and structure.[15] Each of the main divisions may be subdivided into groups or families, the distinction being based mainly upon chemical composition, structure, and mode of occurrence. The four chief families are:

First, aqueous rocks, formed mainly through the agency of water as chemical precipitates or as sedimentary beds.

Second, aeolian rocks, formed from wind-drifted materials.

Third, metamorphic rocks, changed from their original condition through dynamic or chemical agencies, and which may have been partly of aqueous and partly of igneous origin.

Fourth, igneous or eruptive rocks, which have been brought up from below in a molten condition, and which owe their present structural peculiarities to variations in composition and conditions of solidification.

35. **Aqueous Rocks.**—Aqueous rocks may be divided into the following general classes:

First, rocks formed as chemical precipitates.

Second, rocks formed as sedimentary deposits and fragmental in structure. The second class may again be subdivided into rocks formed by mechanical agencies and mainly of inorganic materials; and second, rocks composed mainly of the débris of plant and animal life.

In regard to the first form of aqueous rocks, namely, those formed as chemical precipitates, it may be said that while their quantity is not large they are yet of considerable importance from an agricultural point of view. They embrace those substances

[15] Merrill: Smithsonian Report, 1890; Handbook of Geology, 536; Rocks and Soils, 57.

which, having once been in a condition of vapor or aqueous solution, have been deposited or precipitated, either by cooling or by the evaporation of the liquor holding them in solution, or by coming in contact with chemical substances capable of precipitating them. The influence of water as a solvent is perhaps not fully appreciated. Its solvent influence will be noted particularly under the head of weathering or decay of rocks. Its importance, however, in producing stratified rocks has been very great. Water, especially when under great pressure and at a high temperature, has the power of dissolving many minerals. This power is often greatly increased by the mineral matter previously in solution in the water or by the gases which it may contain. As an illustration of the latter property, the solvent action of water charged with carbon dioxid on limestone may be cited.

When mineral matters have been dissolved by the water in the ways mentioned and carried with the water beyond the environment where the solution has taken place, new conditions are found favorable to the precipitation of the dissolved matters. The water, which before may have been very hot, may reach a place where it cools, and being a supersaturated solution, the excess of the material is thrown down.

On the other hand, if the solution be due to the presence of carbon dioxid and the water reach a place where it is exposed to the air or where the pressure to which the absorption of the excess of gas has been due is diminished, the carbon dioxid will escape and the mineral matters which have been dissolved thereby will be precipitated.

The incrustations which often appear around the mouths of springs and the occurrence of stalagmites and stalactites in caves are illustrations of this action.

In respect of the formation of rocks as precipitates from a state of vapor we have scarcely any illustrations excepting in volcanic regions. The rocky materials with which we are generally acquainted are practically non-volatile at the highest temperature which can be secured on the earth's surface, but it is possible that in the interior of the earth the temperature may be so high as to

maintain many substances in a state of vapor, or which would be gases at that high temperature at ordinary pressures.

They may, in this case, become disassociated so that the compounds or elements exist distinctly in a vaporous condition. Such a vapor transported to regions of diminished temperature would first of all on cooling permit a union of the chemical elements forming new compounds less volatile, which, of course, would be at once precipitated.

The rocks and minerals formed possibly in this way which are of some agricultural importance may be classified as follows: Oxids, carbonates, silicates, sulfids, sulfates, phosphates, chlorids, and hydrocarbon compounds, the most important from an agricultural point of view being the phosphates.

The second group of rocks, namely those formed as sedimentary deposits, differ from those just described in that they are comprised mainly of fragmental materials derived from the breaking down of pre-existing rocks. The formation of fragmental rocks includes, therefore, the same processes as are active in the formation of arable soil. They are deposited from water, and are as a rule distinctly stratified.

Through the action of pressure and the heat thereby generated, or simply through the chemical action of percolating solutions, such rocks pass over into the crystalline sedimentary forms known as metamorphic. All metamorphic rocks, however, are not of a sedimentary origin. For instance, by pressure, heat, and the chemical changes thereby induced, granite may be changed into gneiss and the latter would then be a metamorphic rock.

This group of sedimentary rocks and of sedimentary material, either unchanged or metamorphosed, is of vast extent and includes materials of widely varying chemical and mineralogical nature. They form by far the greater portion of the present surface of the earth, even the mountain ranges being composed mainly of this sedimentary material. Indeed, in the whole of this country there is only a comparatively very small extent of igneous or irruptive rocks. The sedimentary rocks are of great importance from a purely scientific, as well as agricultural viewpoint, since they contain the fossil records of past geological ages.

From them it is possible to study the variations in climate and the meteorological conditions in circumstances and periods far remote, and thus form some idea of the process by which the crust of the earth has been modified by natural forces from its original form to the present time.

36. **Classification of Sedimentary Rocks.**—The sedimentary rocks may be divided, as described by Merrill, with sufficient accuracy for our purposes, into two great classes: First, rocks formed by mechanical agencies and mainly of inorganic materials. These are subdivided again as follows:

(a) The arenaceous group.

(b) The argillaceous group.

(c) The volcanic group.

The second class of sedimentary rocks is formed largely, or in part at least, by mechanical agencies, but is comprised chiefly of the débris of plant and animal life. It may be subdivided as follows:

(d) The siliceous group, such as infusorial earth.

(e) The calcareous group, fossiliferous formations, limestone, etc.

(f) The carbonaceous group, such as peat, lignite, coals, etc.

(g) Phosphatic deposits.

The different classes of rock described above are distinguished by special qualities represented largely by the name.

(a) The first division, the arenaceous group, is composed mainly of the siliceous or coarsely granular materials derived from the disintegration of older crystalline rocks, which have been rearranged in beds of varying thickness through the mechanical agency of water. They are, in short, consolidated or unconsolidated beds of sand and gravel. In composition and texture they vary almost indefinitely. Many of them having suffered little during the process of disintegration and transportation are composed essentially of the same materials as the rocks from which they were derived.

The sandstones, which are the type of these rocks, vary greatly

in structure as well as in composition, in some the grains being rounded while in others they are sharply angular.

The microscopic structure of sandstone is shown in figure seven.[16]

The substance by which the individual grains of a sandstone are bound together is usually the material of some of the other classes, the calcareous, ferruginous, and siliceous cements being the most usual binding agents. This cementing substance is deposited among the granules forming the sandstone by percolating water.

The colors of sandstone are dependent usually upon iron oxids. Especially is this true of the red, brown, and yellow colors. In some of the light grey varieties, the color is that of the minerals comprising the stone. Some of the darker colored sandstones contain organic matter.

(b). The rocks of the argillaceous group are composed essentially of a hydrous silicate of alumina, which is the basis of common clay, and varying amounts of free silica, oxids of iron and manganese, carbonates of lime and magnesia, and small quantities of organic matter. They may have originated *in situ* from the decomposition of feldspars or as deposits of fine mud or silt at the bottom of large bodies of water. The older formations of these rocks are known as shales, argillites and slates and the fissile structure which enables them to be split into thin sheets is probably due to the conditions under which they have been formed and not to any properties of the clay themselves.

One of the purest forms of this rock is kaolin, which is almost a pure hydrous silicate of alumina formed from the decomposition of feldspathic rocks from which the alkalies and other soluble constituents have been removed by water.

(c). Under the volcanic group are included the materials ejected from volcanic vents in a more or less finely comminuted condition and which through the drifting power of atmospheric currents may be scattered over many square miles of territory. Various names are applied to such products, names dependent in

[16] Photomicrograph, Road Material Laboratory, Bureau of Chemistry (Howard & Lord).

large part upon their state of subdivision. Volcanic dust or ashes, includes the finer dust-like or sand-like materials, and lapilli, or rapilli, the coarser. The general name tuff, or tuffa, includes the more or less compacted and stratified beds of this material, while trass, peperino, and pozzuolana are local varietal names given to similar materials occurring in European volcanic regions.[17]

The second division, namely sedimentary rocks composed of the débris of plant and animal life includes many forms of great agricultural importance.

(d) The first subdivision of this group is the infusorial or diatomaceous earth. It forms a fine white or yellowish pulverulent rock composed mainly of minute shells, or tests of diatoms, and is often so soft and pliable as to crumble readily between the thumb and fingers. The beds are of comparatively limited extent, and for this reason are of little agricultural value, although the weathering of this diatomaceous material gives rise to a light yellow clay forming very fertile agricultural lands. Diatomaceous earth has many technical uses such as in filtering and as an absorbent for nitroglycerine.

(e) The second subdivision of this group includes the rocks of a calcareous nature derived from animal life; that is to say, what are properly called limestones. They vary in color, structure, and texture almost indefinitely, and include all possible grades of materials from those which can be used only as a flux, or for lime burning, through ordinary building materials to the finest marbles. These rocks are world-wide in their distribution and limited to no one particular geological era, but are found in stratified beds among deposits of all ages from the most ancient to the most recent.

Owing to the fact that their chief constituent, carbonate of lime, is soluble in ordinary meteoric waters, the rocks have undergone extensive decomposition, their lime being removed, while their less soluble constituents or impurities remain to form one of the chief constituents of soil. A single ton of residual soil represents not infrequently the residue of 100 tons of original rock matter. As this mass of lime carbonate is removed by solution

[17] Merrill: Rocks and Soils, 140.

the residual soil settles, and as the limestone rocks are more soluble than the adjacent rock formations limestone formations usually form valley lands with ridges on either side. Caves are frequently found in such formations. Furthermore, as the lime is almost all in the form of the easily soluble lime carbonate it can be very completely removed and the fertile "limestone soils" are often very deficient in lime and respond readily to an application of burnt lime, which, not infrequently, is quarried from the same field. From an agricultural standpoint this group is of very great interest and importance. The celebrated blue grass soils of Kentucky have been formed in the above manner and geologists are of the opinion that by progressive solution of the limestone the surface of the earth in that locality is now far below the position it originally held.

(f) The third subdivision of this group, namely, that of vegetable origin, includes peat, lignite, coals, etc. Rocks of this group are made up of more or less fragmental remains of plants. In many of them, as the peats and lignites, the traces of plant structure are still apparent. In others, as the anthracite coals, these structures have been wholly obliterated by metamorphic changes.

Plants when decomposing on the surface of the ground give off their carbon to the atmosphere in the shape of carbon dioxid gas leaving only the strictly inorganic or mineral matter behind. When, however, they are protected from oxidizing influences by water or by other plant growth, decomposition is greatly retarded, and a large portion of the carbonaceous and volatile matters is retained, and under pressure from the overlying mass, the material becomes slowly converted into coal. When this process goes on near the surface of the earth, and without much pressure, peat is the product.

(g) The fourth subdivision of this group, the phosphatic, forms a class of rocks limited in extent but of the greatest economic importance. Guano, coprolites, and phosphatic rocks (the phosphorites) come under this head.

37. **Aeolian Rocks.**—This class of rocks is of less importance than the others, either geologically or agriculturally. It is formed

from materials drifted by the winds and this material has various degrees of compactness. Usually the components of these drifts form rocks or deposits of a friable texture and of a fragmental nature. The very extensive deposits of loess in China, forming the most fertile lands, are admitted to have been formed in this way, but it is now generally conceded that similar deposits in this country are of subaqueous origin.

Chief among these rocks, are the volcanic ashes which are often carried to a long distance by the wind before they are deposited and consolidated into rock masses. Many loose soils may be carried to great distances by the wind, the deposits forming new aggregates. This is particularly the case in arid sandy regions.

38. **Metamorphic Rocks.**—This class of rocks includes all sedimentary or eruptive rocks, which, after their deposition and agglomeration, have been changed in their nature through the action of heat, pressure, or by chemical means. Sometimes these changes are so complete that no indication of the character of the original rocks remains. At other times the changes may be found in all the stages of progress, so that they can be traced from the original fragmental or irruptive to the completely metamorphosed deposit. This is especially true of rocks containing large quantities of lime. In those containing silica, the changes are less readily traced.

The metamorphic rocks may be divided into two subclasses, namely, stratified or bedded, and foliated or schistose.

The rocks of the first class are represented by the crystalline limestones and dolomites. The microstructure of a crystalline limestone is shown in Fig. 4, Plate II. When lime and magnesia occur together in combination with carbon dioxid, the substance is known as dolomite. The chemical nature of these rocks and their soil-forming properties are the same as those of the ordinary, non-metamorphosed limestones and dolomites to which reference has already been made. The subject need not, therefore, be further dwelt upon here.

The second variety of metamorphic rocks is represented by the gneisses and crystalline schists. Gneiss has essentially the same

composition of granite and sometimes can hardly be distinguished from it, except by a microscopic study of its sections, and even then it is sometimes difficult to determine. Frequently a number of new minerals is formed in the metamorphic changes. The microstructure of a gneiss and granite is shown in Figs. 5 and 6. The schists include an extremely variable class of rocks, of which quartz is the prevailing constituent, and which, as a rule, are deficient in potash and other important ingredients of plant food.

39. **Rocks Formed Through Igneous Agencies, or Eruptive Rocks.**—This group includes all those rocks, which, having been at some time in a state of igneous fusion, have been solidified into their present form by a process of cooling. It may be stated, as a general principle, that the greater the pressure under which a rock solidifies and the slower and more gradual the cooling the more perfect will be found the crystalline structure. Hence, it follows that the older and more deep-seated rocks which are forced up in the form of dikes, bosses, or intrusive sheets, into the overlying masses, and which have become exposed only through erosion and removal of the overlying rocks, are the more highly crystalline.

The eruptive rocks are divided into two main groups, *viz.:*

(a) Intrusive or plutonic rocks, and

(b) Effusive or volcanic rocks.

Among the more important of the first division of the plutonic form, from an agricultural point of view, are the granites. The essential constituents of granite are quartz, potash feldspar, and plagioclase. One or more minerals of the mica, amphibole or pyroxene groups are also commonly present, and in microscopic proportions apatite and particles of magnetic iron. The more valuable constituents, from an agricultural standpoint, are the minerals potash feldspar, and apatite, which furnish by their decomposition potash and phosphoric acid.

In addition to the granites, which have already been mentioned, the group includes the syenites, the nepheline syenites, the diorites, the gabbros, the diabases, the theralites, the peridotites, and the pyroxenites.

The second group, the effusive or volcanic rocks, includes those igneous rocks, which, like the first group, have been forced up through the overlying rocks, but which were brought to the surface, flowing out as lavas. These, therefore, represent, in many cases, only the upper or surface portions of the first group, differing from them structurally, because they have cooled under little pressure and more rapidly, and hence are not so distinctly crystalline. These rocks according to age, are divided into two groups, the corresponding members of which are given below.[18]

EFFUSIVE OR VOLCANIC ROCKS

Paleovolcanic.	*Neovolcanic.*
Quartz porphyries.	Liparites.
Quartz free porphyries.	Trachytes.
Phonolites.	Phonolites.
Porphyrites.	Andesites.
Melaphyrs and augite porphyrites.	Basalts.
Picrite porphyrites.	Limburgites.

It is, in most cases, impossible to state which of the above classes is of most importance from an agricultural standpoint, since, in the process of soil formation, both chemical and physical processes are involved, whereby the character of the resultant soil is so modified as to but remotely resemble its parent rock. Many soils of volcanic origin are highly fertile and also basic rather than acidic in their constitution.[19] In most soils, the prevailing constituent is the least soluble one of the rock mass from which it was derived. Thus a limestone soil may contain upwards of 90 per cent. of silica and alumina, while the original limestone itself may not have carried more than one or two per cent. of these substances. Of course, if a rock mass contains none of the constituents essential to plant growth, its resultant soil must by itself alone be quite barren. It does not absolutely follow, however, that those rocks containing the highest percentages of valuable constituents will yield the most fertile soils, since much depends on the manner in which they have been formed, and the amount of leaching to which they may have been exposed. Nevertheless, the study of the composition of the rocks in their

[18] Merrill: Rocks and Soils, 63.

[19] Maxwell: Lavas and Soils of the Hawaiian Islands, 61.

relations to soils, is an extremely interesting and by no means unfruitful one.

40. Chemical Composition of Rocks.—The more important elements occurring in rocks and the proportions in which they exist are given in the table below:[20]

	A.	B.	C.	D,	E.	F.	G.
SiO_2	55.43	60.15	58.38	78.66	84.86	5.19	14.09
TiO_2	.46	.76	.65	.25	.41	.06	.08
Al_2O_3	13.84	16.45	15.47	4.78	5.96	.81	1.75
Fe_2O_3	4.00	4.04	4.03	1.08	1.39	} .54	} .77
FeO	1.74	2.90	2.46	.30	.84	} undet.	} undet.
MnO	trace	trace	trace	trace	trace	.05	.03
CaO	5.96	1.41	3.12	5.52	1.05	42.61	40.60
SrO	none	none	none	trace	none	none	none
BaO	.06	.04	.05	.05	.01	none	none
MgO	2.67	2.32	2.45	1.17	.52	7.90	4.49
K_2O	2.67	3.60	3.25	1.32	1.16	.33	.58
Na_2O	1.80	1.01	1.31	.45	.76	.05	.62
Li_2O	trace	trace	trace	trace	trace	trace	trace
H_2O at 110°	2.11	.89	1.34	.31	.27	.21	.30
H_2O above 110°	3.45	3.82	3.68	1.33*a*	1.47*a*	.56*a*	.88*a*
P_2O_5	.20	.15	.17	.08	.06	.04	.42
CO_2	4.62	1.46	2.64	5.04	1.01	41.58	35.58
S	.....	.....	.....	.....	.....	.09	.07
SO_3	.78	.58	.65	.07	.09	.05	.07
Cl	.....	.....	.....	trace	trace	.02	.01
Carbon *b*	.69	.88	.81	.....	.....	.....	.....
	100.48	100.46	100.46	100.41	99.86	100.09	100.34

a Includes organic matter.
b Of organic origin.

The character of the rocks and the number of analyses from which the mean composition has been calculated are as follows:

A. Composite analysis of 27 Mesozoic and Cenozoic shales. Each individual shale was taken in amount roughly proportional to the mass of the formation which it represented.

B. Composite analysis of 51 Paleozoic shales, weighted as in the former case.

C. General average of A and B, giving them, respectively, weights as 3 to 5. This average represents 78 rocks.

D. Composite analysis of 253 sandstones, about 1 gram of each entering into the average sample.

[20] Clarke: Bulletin No. 228 U. S. Geological Survey, 1904, 20–21.

E. Composite analysis of 371 sandstones used for building purposes, equal weights of each.

F. Composite analysis of 345 limestones, equal weights of each.

G. Composite analysis of 498 limestones used for building purposes, equal weights of each.

GENESIS OF SOILS.

41. **Origin of Soils.**—The soils in which crops grow and which form the subject of the analytical processes to be hereinafter described have been formed under the combined influences of rock decay and plant and other organic growth. The mineral matters of soils have had their origin in the decay of rocks, while the humic and other organic constituents have been derived from living bodies. It is not the object of this treatise to discuss in detail the processes of soil formation, but only to give such general outlines as may bear particularly on the proper conceptions of the principles of soil investigation.

42. **The Decay of Rocks.**—The origin and composition of rocks are fully set forth in works on geology and mineralogy. Only a brief summary of those points of interest to agriculture has been given in the preceding pages. The soil analyst should be acquainted with these principles, but for practical purposes he has only to understand the chief factors active in securing the decay of rocks and in preparing the débris thereof for plant growth.

The following outline is based on the generally accepted theories respecting the formation of soils.

The forces ordinarily concerned in the decay of rocks are:

1. Changes of temperature, including the ordinary daily and monthly changes, and the conditions of freezing and thawing.
2. Moving air, water and ice.
3. Chemical action of water and air.
4. Influence of vegetable life:
   (a) Shading the rock or soil surface;
   (b) Penetrating the rock or partly decomposed material with its roots, thus admitting air;

(c) Solvent action of roots ;

(d) Chemical action of decaying organic matter.

5. Earth worms.

6. Bacteria.

43. The Action of Freezing and Thawing.—In those parts of a rock stratum exposed near the surface of the earth the processes of freezing and thawing have perhaps had considerable influence in rock decay. The expansive force of freezing water is well known. Ice occupies a larger volume than the water from which it is formed. The force with which this expansion takes place is almost irresistible. The phenomenon of split water pipes which have been exposed to a freezing temperature is not an uncommon one. While the increase in volume is not large, yet it is entirely sufficient to produce serious results. The way in which freezing affects exposed rock is easily understood. The effect is unnoticeable if the rock be dry. If, on the other hand, it be saturated with water, the disintegrating effect of a freeze must be of considerable magnitude. This effect becomes more pronounced if the intervals of freezing and thawing be of short duration. The whole affected portion of the rock may thus become thoroughly decayed. But even in the most favorable conditions this form of disintegration must be confined to a thin superficial area. Even in very cold climates where agricultural pursuits are possible the frost only penetrates a few feet below the surface, and therefore the action of ice cannot in any way be connected with those changes at considerable depths, to which the superficial cover of the earth is obnoxious. Nevertheless, certain building materials seem very sensitive to this sort of weathering, and the crumbling of many building stones is due chiefly to this cause.

On the whole it appears that the action of ice in producing rock decay has been somwhat overrated, although its power must not by any means be denied. But on the other hand a freeze extending over a long time tends to preserve the rocks, and it therefore appears that the entire absence of frost would promote the process of rock decay. If this be true, other things being equal, the decay of the earth's surface would extend to greater depths in

equatorial than in polar regions. Many observed facts tend to corroborate this theory.

At best it must be admitted that frost has affected the earth's crust only to an insignificant depth, but its influence in modifying the arable part of the soil in temperate climate is of great importance to agriculture.

44. The Action of Glaciers.—The action of ice in soil formation is not confined alone to the processes just described. At a period not very remote geologically, a great part of our Northern States was covered with a vast field of moving ice. These seas of ice crept down upon us from more northern latitudes and swept before them every vestige of animal and vegetable life. In their movement they leveled and destroyed the crests of hills and filled the valleys with the débris. They crushed and comminuted the strata of rocks which opposed their flow and carried huge boulders of granite hundred of miles from their homes. On melting they left vast moraines of rocks and pebbles which will mark for all time the termini of these empires of ice. When the ice of these vast glaciers finally melted, the surface which they had leveled presented the appearance of an extended plain. No estimate can be made of the enormous quantities of rock material which were ground to finest powder by these glaciers. This rock powder forms to-day no inconsiderable part of those fertile soils which are composed of glacial drift. The rich materials of these soils probably bear a more intimate relation to the rocks from which they were formed than of any other kinds of soil in the world. The rocks were literally ground into a fine powder, and this powder was intimately mixed with the soils which had already been formed *in situ*. The melting ice also left exposed to disintegrating forces large surfaces of unprotected rocks in which decay could go on much more rapidly than when covered with the débris which protected them before the advent of the ice. The area of glacial action extended over nearly all of New England and over the whole area of the northern central tier of States. It extended southward almost to the Ohio river, and in some places crossed it. The effect of the ice age in producing and modifying our soil must never be forgotten in a study of soil genesis. It is not a part

of our purpose here to study the causes which produced the age of ice. Even a brief reference to some of the more probable ones might be entirely out of place. Before the glacial period it is certain that a tropical climate extended almost, if not quite, to the North Pole. The fossil remains of tropical plants and animals which have been found in high northern latitudes are abundant proofs of this fact.

In the opinion of Sterry Hunt rock decay has taken place largely in preglacial and pretertiary times.[21] The decay of crystalline rocks is a process of great antiquity. It is also a universal phenomenon. The fact that the rocks of the southern part of this country seem to be covered with a deeper débris than those further north may be due in part to the mechanical translation of the eroded particles towards the south. The decay and softening of the material were processes necessarily preceding the erosion by aqueous and glacial action.

It is possible also that a climate may have existed in the earlier geological ages more favorable to the decay of rocks than that of present time.

45. Progress of Decay as Affected by Latitude.—Extensive investigations carried on along the Atlantic side of the country show wide differences in the rate of decay in the same kind of rocks in different latitudes. In general, the progress of decay is more marked toward the south. The same fact is observed in the great interior valleys of the country; at least, everywhere except in the arid and semi-arid regions. Wherever there is a deficiency of water the processes of decay have been arrested. Where the rock strata have been displaced from a horizontal position the progress of decay has been more rapid. This is easily understood. The percolation of water is more easy as the displacement approaches a vertical position.

A most remarkable example of this is seen in the rocks of North Carolina.[22] A kind of rock known as trap is found in layers called dikes in the Newark system of rocks in that State. These dikes have been so completely displaced from the horizon-

[21] Mineral Physiology and Physiography, 251.

[22] Bulletin No. 52 U. S. Geological Survey, 16.

tal position they at first occupied as to have an almost vertical dip. The edges thus exposed vary from a few feet to nearly 100 feet in thickness. The trap rock in those localities is composed almost exclusively of the mineral dolerite, which is so hard and elastic in a fresh state as to ring like a piece of metal when struck with a hammer. In building a railroad through this region these dikes were in some places uncovered to a depth of forty feet and more. At this depth they were found completely decomposed and with no indications of having reached the lower limit of disintegration. The original hard bluish dolerite has been transformed into a yellowish clay-like mass that can be molded in the fingers and cut like putty. Similar geological formations in New Jersey and further North do not exhibit anything like so great a degree of decomposition, thus illustrating in a marked degree the fact that freezing weather for a part of the year is a protection against rock decay. The ice of winter at least protects the rocks from surface infiltration, although it can not stop the subterranean solution which must go on continuously.

Other things being equal, therefore, it appears that as the region of winter frost is passed the decay of the rocks has been more rapid, because water, the chief disintegrating force, acts more constantly.

46. The Solvent Action of Water.—The water of springs and wells is not pure. It contains in solution mineral matters and often a trace of organic matter. The organic matter comes from contact with vegetable matter and other organic materials near the surface of the earth. The mineral matter is derived from the solvent action of the water and its contents on the soil and rocks.

The expression "hard" or "soft" applied to water indicates that it has much or little carbonate of lime and magnesia or sulfates of the same bases in solution. Water containing much carbonate of lime (or lime and magnesia) in solution is usually more or less charged with carbon dioxid. When boiled this gas is driven off and the carbonates precipitated. This kind of hardness is called temporary. When surface and spring waters are collected into streams and rivers they still contain in solution the greater part of the mineral matters which they at first carried.

Fig. 8.

View West of Chevy Chase, Maryland.

The fresh granite rock is shown passing upward into material more and more decomposed until it becomes sufficiently pulverized and soluble to support plant life. The roots showing in the upper part of the picture formerly penetrated the decomposed rock, but have been exposed through grading operations.

Photograph by E. E. Ewell, 1895.

When waters have more than 600 parts of mineral matter per million they are not deemed suitable for drinking waters. Mineral waters, so called, are those which carry large quantities of mineral matter, or which contain certain comparatively rare mineral substances which are valued for their medicinal effects.

The analysis of spring, well, or river waters will always give some indication of the character of the rocks and soils over or through which they have passed. The vast quantities of mineral matters carried into oceans and seas are gradually deposited as the water is evaporated. If, however, these matters be very soluble, such as common salt, sulfate of magnesia, etc., they are found in concentrated solutions as is seen in sea waters. In small bodies of waters, such as inland seas, which have no outlet, this concentration may proceed to a much greater extent than in the ocean. As an instance of this, it may be noted that the waters of the Dead Sea and Great Salt Lake are impregnated to a far greater degree with soluble salts than the water of the ocean. The solvent action of water on rocks is greatly increased by the traces of organic (or carbonic) acids which it may contain. When surface water comes in contact with vegetable matter it may become partially charged with the organic acids which the growing vegetables may contain or decaying vegetable matter produce. Such acids coming in contact with limestone under pressure will set free carbon dioxid. Water charged with carbon dioxid acts vigorously as a solvent on limestone and some other mineral aggregates. If such waters penetrate deeply below the surface of the earth their activity as solvents may be greatly increased by the higher temperature to which they are subjected. Hence, all these forces combine to disintegrate the rocks, and through such agencies vast deposits of original and secondary rocks have been completely decomposed. The decay of nitrogenous matters gives rise to nitric acid which also adds to the disintegrating power of percolating waters. The gradual passing of the firm rock into an arable soil is beautifully shown in Fig. 8.

Hilgard has called attention to the fact that soils formed with a small suply of water as in the arid regions have a distinctive sandy character, while those formed under the

influence of an abundant supply of water contain more clay.[23] In the decay of rocks therefore a dry climate has a distinctly retarding effect on the kaolinization of feldspathic rocks. The soils formed *in situ* on the Atlantic border are therefore chiefly clay loams, while on the Pacific border they contain a larger quantity of sand.

47. **Action of Vegetable Life.**—The preliminary condition to the growth of vegetation is the formation of soil, but once started, vegetation aids greatly in the decomposition of rocks. Some forms of vegetation, as the lichens, have apparently the faculty of growing on the bare surface of rocks, but the higher orders of plants require at least a little soil. Vegetation acts as a rock disintegrant by shading the surface and thus rendering the action of water more effective, by mechanically separating the rock particles by means of its penetrating roots and by the positive action of the root juices. The rootlets of plants in contact with limestone or marble dissolve large portions of these substances, and while their action on more refractory rocks is slower, it must be of considerable importance. It is evident that the solvent action of the acids of living plants is confined almost exclusively to the particles of rocks proximate to points of exudation. The organic matter introduced into the soil by vegetation also promotes decay still further both directly and by the formation of acids of the humic series. This matter also furnishes a considerable portion of carbon dioxid which is carried by the water and assists in its solvent action.

48. **Action of Earth-Worms.**—Of animal organisms those most active in the formation of soil are earth-worms. The work of earth-worms in soil forming has been exhaustively studied by Darwin.[24] The worms not only modify the soil by bringing to the surface portions of the subsoil, but also influence its physical state by making it more porous and pulverulent. According to Darwin the intestinal content of worms has an acid reaction, and this has an effect on those portions of the soil passing through their alimentary

[23] Report California Agricultural Experiment Station, 1892, 107.

[24] The Formation of Vegetable Mold through the Action of Worms.

canal. The acids, which are formed in the upper part of the digestive canal are neutralized by the carbonate of lime secreted by the calciferous glands of the worms thus neutralizing the free acid and changing the reaction to alkaline in the lower part of the canal.

The worms further modify the composition of the soil by drawing leaves and other organic matter into their holes, and leaving therein a portion of such matter which is gradually converted into humus. A striking illustration of this process is found in an experiment by von Hensen.[25] Darwin estimates that about 11 tons of organic matter per acre are annually added to the soil in regions where worms abound. A considerable portion of the ammonia in the soil at any given time may also be due to the action of worms, as much as 0.18 per cent. of this substance having been found in their excrement. It is probable that nearly the whole of the vegetable matter in the soil passes sooner or later through the alimentary canals of these ceaseless soil builders, and is converted into the form of humus. Finally the bodies of the worms serve to increase the quantity of the organic matter in the soil.

49. Action of Bacteria.—The intimate relations which have been found to subsist between certain minute organisms and the chemical reactions which take place in the soil is a sufficient excuse for noting the effect of other similar organisms in the formation of soils.

In addition to the usual forces active in decomposing rocks Müntz has described the effects of a nitrifying bacillus contributing to the same purpose.[26]

According to him the bare rock usually furnishes a purely mineral environment where organisms cannot be developed unless they are able to draw their nourishment directly from the air. Some nitrifying organisms belong to this class. It has been shown that these bodies can be developed by absorbing from the ambient atmosphere carbonate of ammonia and vapors of alcohol, the presence of which has been observed in the air. According to the observations of Winogradsky, they assimilate even

[25] Stockbridge: Rocks and Soils, 131.

[26] Comptes rendus, 110 : 1370.

the carbon of the carbon dioxid just as the parts of plants which contain chlorophyl. Thus even on the denuded rocks of high mountains the conditions for the development of all these inferior organisms exist. In examining the particles produced by attrition, it is easily established that they are uniformly covered by a layer of organic matter evidently formed by microscopic vegetation. Thus we see, in the very first products of attrition, appearing upon the rocky particles the characteristic element of vegetable soil, *viz.*, humus, the proportion of which increases rapidly with the products of disaggregation collected at the foot of declivities until finally they become covered with chlorophyliferous plants.

In a similar manner the presence of nitrifying organisms has been noted upon rocky particles from high attitudes received in sterilized tubes, and where these are sown in an appropriate environment they soon produce colonies. The naked rocks of the Alps, the Pyrenees, the Auvergnes and the Vosges, comprise mineralogical types of the most varied nature, *viz.*, granite, porphyry, gneiss, mica-schist, volcanic rocks and limestones and all these have shown themselves to be covered with the nitrifying ferment. It is known that below a certain temperature these organisms are not active; their action upon the rock is, therefore, limited to the summer period. During the cold season their life is suspended but they do not perish, inasmuch as they have been found living and ready to resume all their activity after an indefinite sleep on the ice of the glaciers where the temperature is never elevated above zero.

The nitrifying ferment is exercised on a much larger scale in the normal conditions of the lower levels where the rock is covered with earth. This activity is not limited to the mass of rock but is continued upon the fragments of the most diverse size scattered through the soil and it helps to gradually reduce them to a state of fine particles. The action of these ferments is therefore a phenomenon of the widest extension.

The action of these micro-organisms according to Müntz is not confined to the surface but extends to the most interior particles of the rocky mass. Where, however, there is nothing of

a nitrogenous nature to nitrify such an organism must live in a state of suspended animation unless it is able to act on the nitrogen of the air.

When the extreme minuteness of these phenomena is considered there may be a tendency to despise their importance, but their continuity and their generality in the opinion of Müntz place them among the geological causes to which the crust of the earth owes a part of its actual physiognomy and which particularly have contributed to the formation of the deposits of the comminuted elements constituting arable soil.

The general action of nitrifying organisms in the soil, the nature of these bodies, and the method of isolating and identifying them will be fully discussed in another part of this work. Brauner calls attention to the danger of overestimating the activity of nitrifying organism in effecting the decay of rocks due to their inability to live at great depths.[27] As is well known they diminish in abundance as the depth below the surface increases and disappear, or at least are inactive at depths of from three to six feet. Brauner says that in these cases the statements of specialists are the only safe reliance and the finding of bacteria in rocks by any one not a specialist is to be regarded with suspicion. Only those who have worked in bacteriology can fully appreciate the difficulties to be enumerated and the precautions to be taken in dealing with those organisms in order to prevent being misled by faulty manipulation.

50. Action of the Air.—The air itself takes an active part in rock decay. Wherever rocks are exposed to decay, there air is found or, at least, the active principle of air, *viz.*, oxygen. The air as a gas not only penetrates to a great depth in the earth, but is also carried to much greater depths by water which always holds a greater or less quantity of air in solution. The oxygen of the air is thus brought into intimate contact with the disintegrating materials and is present in a condition to assist wherever possible in the decomposing processes.

The oxygen acts vigorously on the lower oxids of iron, converting them into peroxids, and thus tends to produce decay.

[27] American Journal of Science, [4], 8 : 438.

There are other constituents of rocks which oxygen attacks and thus helps to their final breaking up. It is true that, as a rule, the constituents of rocks are already oxidized to nearly as high a degree as possible, and on these constituents of course the air would have no effect. But on others, especially when helped by water with the other substances it carries in solution, the air may greatly aid in the work of destruction.

In a general view, the action of the air in soil formation may be regarded as of secondary importance, and to depend chiefly on the oxidation of the lower to the higher basic forms. These processes, while they seem of little value, have, nevertheless, been of considerable importance in the production of that residue of rock disintegration which constitutes the soil.

51. Classification of Soil According to Deposition.—In regard to their method of deposition soils are divided into five classes:

1. Those which are formed from the decomposition of crystalline or sedimentary rocks or of unconsolidated sedimentary material *in situ.*

2. Those which have been moved by water from the place of their original formation and deposited by subsidence (bottom lands, alluvial soils, lacustrine deposits, etc.).

3. Those which have been deposited as débris from moving masses of ice (glacial drift).

4. Soils formed from volcanic ashes or from materials moved by the wind and deposited in low places or in hills or ridges.

5. Those formed chiefly from the decay of vegetable matter, (tule, peat, etc.).

52. Qualities of Soils.—In respect of quality, soils have been arbitrarily divided into many kinds. Some of the more important of these divisions are as follows:

1. *Sand.* Soils consisting almost exclusively of sand.

2. *Sandy Loams.* Soils containing some humus and clay but an excess of sand.

3. *Loams.* Soils inclining neither to sand nor clay and contain-

ing considerable portions of vegetable mold, being very pulverulent and easily broken up into loose and porous masses.

4. *Clays.* Stiff soils in which the silicate of alumina and other fine mineral particles are present in large quantity.

5. *Marls.* Deposits containing an unusual proportion of carbonate of lime, with often some potash or phosphoric acid derived from the remains of sea-animals and plants. It is generally supposed that marls are mixtures more or less intimate of calcium carbonate and clay.[28] In general a clay is a definite mixture of silica with hydrous aluminum silicate having a composition $2SiO_2,Al_2O_3 + H_2O$. This compound is characterized by the temperature at which it suffers dehydration, *viz.*, about 600° and a marked disengagement of heat which takes place at about 950°. The residue obtained by dissolving a marl in acetic acid never presents the characteristic properties of a typical clay. It is richer in silica and its temperature of dehydration is far inferior. Moreover it does not give any sudden disengagement of heat at elevated temperatures. It is sometimes atmorphous, sometimes crystallized, but in this case its crystalline structure is quite different from that of clay particles.

6. *Alkaline.* Soils containing carbonate and sulfate of soda, or an excess of these alkaline and other soluble mineral substances.

7. *Adobe.* A fine grained porous earth of peculiar properties hereinafter described.

8. *Vegetable.* Soils containing much vegetable débris in an advanced state of decomposition. When such matter predominates or exists in large proportion in a soil the term tule or peat is applied to it.

With the exception of numbers six, seven and eight these types of soil are so well-known as to require no further description for analytical purposes. The alkaline, adobe and vegetable soils on the contrary demand further study.

53. Alkaline Soils.—The importance of a more extended notice of this class of soils for analytical purposes is emphasized by their large extent in the United States.

[28] Le Chatelier: Comptes rendus, 1894, **118** : 262.

Chiefly through the researches of Hilgard attention has been called to the true character of these soils which are found throughout a large part of the Western United States and which are known by the common name of aikali.[29] The following description of the origin of these soils is compiled chiefly from Hilgard's papers on this subject. Wherever the rain-fall is scanty, and especially where the rains do not come at any one time with sufficient force to thoroughly saturate the soil and carry down through the subsoil and off through the drainage waters the alkali contained therein, favorable conditions exist for the production of the alkaline soil mentioned above. The peculiar characteristic of this soil is the efflorescence which occurs upon its surface and which is due to the raising of soluble salts in the soil by the water rising through capillary attraction and evaporating from the surface, leaving the salts as an efflorescence.

Soils which contain a large amount of alkali are usually very rich in mineral plant food, and if the excess of soluble salts could be removed, these lands under favorable conditions of moisture and temperature would produce large crops.

The formation of the alkali may be briefly described as follows: By the decomposition of the native rocks, certain salts soluble in water are formed. These salts in the present matter are chiefly sodium and potassium sulfates, chlorids and carbonates. The salts of potash together with those of lime are more tenaciously held by the soil than the soluble salts of soda, and the result of this natural affinity of the soil for soluble potash, lime and magnesian salts is seen in the formation at the surface of the earth, by the process of evaporation above described, of a crust of alkaline material which is chiefly composed of the soluble salts of soda. In countries which have a sufficient amount of rain-fall, these soluble salts are carried away either by the surface drainage or by the percolation of water through the soil, and the sodium chlorid is accumulated in this way in the waters of the ocean. But where a sufficient amount of rain-fall does not occur, these soluble

[29] Bulletins California Agricultural Experiment Station Nos. 28, 53, 83, 105, 108, 121, 133, 140; Annual Reports of Station: 1885, 27; 1890, 87; 1892, 140; 1897, 8; 1898, 21; 1901, 37.

salts carried down by each shower only to a certain depth rise again on the evaporation of the water, reinforced by any additional soluble material which may be found in the soil itself. The three most important ingredients of the alkali of the lands referred to are sodium chlorid, sulfate, and carbonate. When the latter salt, namely, sodium carbonate, is present in predominant quantity, it gives rise to what is popularity known as black alkali. This black color is due to the dark colored solution which sodium carbonate makes with the organic matters or humus of the soil. The black alkali is far more injurious to growing vegetation than the white alkali composed chiefly of sodium sulfate and chlorid.

This black alkali has been very successfully treated by Hilgard by the application of gypsum which reacting with the sodium carbonate produces calcium carbonate and sodium sulfate, thus converting the black into the white alkali and adding an ingredient in the shape of lime carbonate to stiff soils which tends to make them more pulverulent and easy of tillage.[30]

This method of treatment, however, as can be easily seen, is only palliative, the whole amount of the alkaline substances being still left in the soil, only in a less injurious form.

The only perfect remedy for alkaline soils, as has been pointed out by Hilgard, is in the introduction of underdrainage in connection with irrigation. The partial irrigation of alkaline soils, affording enough moisture to carry the alkali down to and perhaps partially through the subsoil, can produce only a temporary alleviation of the difficulties produced by the alkali. Subsequent evaporation may indeed increase the amount of surface incrustation. For this reason in many cases the practice of irrigation without underdrainage may completely ruin an otherwise fertile soil by slowly increasing the amount of alkali therein by the total amount of the alkaline material added in the waters of irrigation and brought to the surface by the evaporation of the temporarily deeper percolation of the water.

As Hilgard has pointed out, if a soil can be practically freed from alkali by underdrainage connected with a thorough satura-

[30] California Agricultural Experiment Station, Bulletin No. 83.

tion by irrigation, it may be centuries before the alkali will accumulate in that soil again when ordinary irrigation only is practiced. It may thus become possible to reclaim large extents of alkaline soil little by little by treating them with an excess of irrigation water in connection with thorough underdrainage. The composition of the alkali on the surface of the soil due to the causes above set forth is shown by the analyses of Hilgard and Weber, which follows:[31]

TABLE SHOWING COMPOSITION OF ALKALI SALTS IN SAN JUAQUIN VALLEY

	TULARE COUNTY.					
	Goshen	People's ditch.	Near Lake Tulare.	Visalia	Lemoore	Tulare Expm't Station
	Surface soil.	Alkali crust.	Surface soil.	Surface soil.	Alkali crust.	Alkali crust.
Soluble salts in 100 parts soil	1.40	.....	0.83	1.26	.....	.....
Potassium sulfate	.....	.....	.....	.....	.....	small
a Potassium nitrate	.....	.....	.....	.....	.....	small
Potassium carbonate (saleratus)	.....	.....	.....	18.80	.....	.....
Sodium sulfate (Glauber's salt)	44.24	1.22	31.30 (*n*)	13.4	chiefly	32.8
Sodium carbonate (sal-soda)	32.98	88.09	18.2	45.3	.....	13.16
Sodium chloride (common salt)	16.74	1.00	.....	4.4	little	31.16
a Sodium phosphate	1.97	.....	0.22	10.4	.....	.....
Calcium sulfate (gypsum)	.. ..	.....	.....	.....	little	.....
Magnesium sulfate (Epsom salt)	.....	.....	.....	8.1	moderate	.....
Organic matter	1.97	9.21	7.5	.....	.....	5.37

a Very generally present, but not always in quantities sufficient for determination.

54. Equilibrium Reactions in Solutions of Alkali.—According to Cameron the classification of alkali into black and white is not entirely satisfactory for practical purposes.[32] He suggests a tentative classification according to the predominating reactions which take place in aqueous solutions of the alkali. Where common salt and sulfate of lime are the chief ingredients the reaction is represented as follows:—

$$CaSO_4 + 2NaCl \rightleftarrows Na_2SO_4 + CaCl_2.$$

The gypsum in this condition becomes more soluble under the influence of the solution of common salt. Where the calcium chlorid which is formed by this reaction reaches the surface in periods of protracted drought, it gives the surface the appearance of being moist, on account of its highly hygroscopic nature. Cal-

[31] Bul. 82, Cal. Ag. Ex. Sta., p. 4.

[32] Bulletin No. 17, Division of Soils, 26.

cium chlorid with organic matter forms a dark color and thus the appearance of black alkali may be simulated, although no soluble carbonates may be present. Another type of reaction which may go on is where calcium carbonate and sodium chlorid are the predominating salts in which case the following reaction takes place:—

$$CaCO_3 + 2NaCl \rightleftarrows Na_2CO_3 + CaCl_2.$$

The calcium chlorid formed in this way would, of course, act as in the previous case. In the presence of carbon dioxid a reaction would take place according to the following formula:—

$$Ca(HCO_3)_2 + NaCl \rightleftarrows CaCl_2 + NaHCO_3.$$

When the carbonate of lime in solution will reach the surface and lose its excess of carbon dioxid it would naturally revert to the normal state. Magnesium carbonate may partly replace the calcium carbonate in a reaction of this kind. If sodium sulfate and calcium carbonate are the predominating salts in the soil the reaction would assume the following form:

$$Na_2SO_4 + CaCO_3 \rightleftarrows Na_2CO_3 + CaSO_4.$$

The class of alkali most commonly encountered is that in which the predominating feature is the simultaneous action of solutions of sodium chlorid upon gypsum and calcium carbonate. In this condition there can only be a small amount of sodium carbonates formed and the solubility of the gypsum is also not as great as when calcium carbonate is not present.

55. **Adobe Soils.**—In many parts of the arid regions of this country which can be recovered for agricultural purposes by irrigation the soil has peculiar characteristics.

The name adobe as commonly used applies to both the sundried bricks of the arid regions of the West and Southwest, and to the materials of which they are composed. The material is described by Russell as a fine grained porous earth, varying in color through many shades of gray and yellow, which crumbles between the fingers, and separates most readily in a vertical direction.[33] The coherency of the material is so great that vertical scarps will stand for many years without forming a noticeable talus slope.

[33] Geological Magazine, 7 : 291–2.

Distribution.—The area over which adobe forms a large part of the surface has not been accurately mapped, but enough is known to indicate that it is essentially co-extensive with the more arid portions of this country. In a very general way it may be considered as being limited to the region in which the mean annual rain-fall is less than twenty inches. It forms the surface over large portions of Colorado, New Mexico, Western Texas, Arizona, Southern California, Nevada, Utah, Southern Oregon, Southern Idaho, and Wyoming. Adobe accurs also in Mexico and may there reach a greater development than in the United States, but observations concerning it south of the Rio Grande are wanting.

In the United States it occurs from near the sea-level in Arizona, and even below the sea-level in Southern California, up to an elevation of at least 6,000 or 8,000 feet, along the eastern border of the Rocky Mountains, and in the elevated valleys of New Mexico, Colorado, and Wyoming. It occupies depressions of all sizes up to valleys having an area of hundreds of square miles. Although occurring throughout the arid region, it can be studied to best advantage in the drainless and lakeless basins in Nevada, Utah, and Arizona.

Composition.—When examined under the microscope, the adobe is seen to be composed of irregular, unassorted flakes and grains, principally quartz, but fragments of other minerals are also present. An exhaustive microscopic study has not been made, but the samples examined from widely-separated localities are very similar. The principal characteristics observed are the extreme angularity of the particles composing the deposit and the undecomposed condition of the various minerals entering into its composition. It is to be inferred from this that the material has not been exposed even to a very moderate degree of friction, and has not undergone subaerial decay before being deposited. Adobe collected, at typical localities is so fine in texture that no grit can be felt when it is rubbed between the fingers; in other instances it contains angular rock fragments of appreciable size.

The composition of the material is illustrated by the following analyses:

ANALYSES OF ADOBE

By L. G. EAKINS,

Constituents.	No. 1. Santa Fe, New Mexico.	No. 2. Fort Wingate, New Mexico.	No. 3. Humboldt, Nevada.	No. 4. Salt Lake City, Utah.
SiO_2	66.69	26.67	44.64	19.24
Al_2O_3	14.16	0.91	13.19	3.26
Fe_2O_3	4.38	0.64	5.12	1.09
MnO	0.09	trace	0.13	trace
CaO	2.49	36.40	13.91	38.94
MgO	1.28	0.51	2.96	2.75
K_2O	1.21	trace	1.71	trace
Na_2O	0.67	trace	0.59	trace
CO_2	0.77	25.84	8.55	29.57
P_2O_5	0.29	0.75	0.94	0.23
SO_3	0.41	0.82	0.64	0.53
Cl	0.34	0.07	0.14	0.11
H_2O	4.94	2.26	3.84	1.67
Organic matter	2.00	5.10	3.43	2.96
	99.72	99.97	99.84	100.35

Judged by the content of calcium carbonate alone three of the above samples resemble marl.

56. Vegetable Soils.—The heavy soils whose origin has been described are essentially of a mineral nature. The quantity of organic matter in such soils may vary from a mere trace to a few per cent., but they never lose their mineral characteristics. When a soil on the other hand is composed almost exclusively of vegetable mold it belongs to quite another type. Such soils are called tule, peat or muck. In this country there are thousands of acres of peat or muck soils; the largest contiguous deposits being found in Southern Florida. The origin of these soils is easily understood. Whenever rank vegetation grows in such a location as to secure for the organic matter formed a slow decay there is a tendency to the accumulation of vegetable mold in shallow water or on marshy ground and where other conditions are favorable to such accumulations. In Florida the peaty soils have been accumulated about the margins of lakes. During the rainy season the marshes bordering these are partly covered with water, but the vegetation is very luxuriant. The water protects the vegetable matter from being destroyed by fire. It therefore accumu-

lates from year to year and is gradually compacted into quite a uniform mass of vegetable mold.

The ultimate composition of the mold is illustrated in the following table which shows the character of the layers at one, two and three feet in depth:[34]

	Carbon.	Hydrogen.	Nitrogen.	Volatile matter.
1 foot....	57.67 per cent.	4.48 per cent.	2.24 per cent.	90.60 per cent.
2 feet....	47.07 "	5.15 "	1.40 "	72.00 "
3 feet....	8.52 "	0.53 "	0.31 "	15.00 "

In this last sample, the mold was only three feet deep, resting on pure sand. As the bottom of the deposit is approached the admixture of sand becomes greater and the percentage of organic matter less.

No reliable estimate of the time which has been required to form these deposits can be given, but in the Okeechobee region in Florida the deposit of vegetable mold in some places exceeds ten feet in depth.

The purest vegetable or peat soils contain only small quantities of potash and phosphoric acid, and especially is this true of the Florida deposits which have been formed of vegetable growth containing very little mineral matter.

It is not at all probable that the flora now growing on any particular area of virgin peat contains all the plants that have contributed to its formation. The principal vegetable growths now going to make up the peat soils of Florida are the following:

Common names.	Botanical names.
Saw grass	Cladium effusum.
Yellow pond lily	Nymphea flava.
Maiden cane grass	Panicum Curtisii.
Alligator Wampee	Pontederia cordata.
Sedge	Cyperus species.
Fern brake	Osmunda "
Mallow	Malva "
Broom sedge	Andropogon "
Arrow Weed	Sagittaria "

The above are only the plants growing in the greatest profu-

[34] Wiley: Agricultural Science, 1893, 106 et seq.

sion and do not include all which are now contributing to increase the store of vegetable débris.

57. **Humus.**—The active principle of vegetable mold is called humus, a term used to designate in general the products of the decomposition of vegetable matter as they are found in soils. In peat and vegetable soils are found a mixture of humus with undecomposed or partially decomposed vegetation.

According to Kostyschoff vegetable matter decays under the influence of molds and bacteria.[85] Molds alone produce the dark colored matters which give soils rich in vegetable matter, their color. One chief characteristic of humus is its richness in nitrogen. Black Russian soil contains from 4 to 6.65 per cent. of nitrogen. This soil is estimated to contain 60,000,000 organisms per gram and much of the nitrogen which it holds must be in the form of proteid derivatives. The first development in decaying vegetable matter is of bacteria and there is a tendency of the decaying matter to become acid. This causes the death of the bacteria and the ammonia produced thereby neutralizes the acid. The various kinds of mold grow when the reaction becomes neutral. Afterwards the bacteria and the molds develop together. This statement of Kostychoff is not a very satisfactory explanation of even our limited knowledge of the decomposition of organic matters in the soil. Ammonia and ammonia salts are formed not by the decay of some forms of bacteria but by the activities of other forms. It has been found that in nitrification there are three distinct forms of bacteria concerned in the final products of ammonia, nitrites, and nitrates. Humus always contains easily decomposable matter and consequently the rate of decay in similar conditions at any observed periods is nearly the same. In humus which is produced above the water-level Kostytchoff states that all trace of the vegetable structure is destroyed by the leaves being gnawed and passed through the bodies of caterpillars and wire-worms. Under the water-level the vegetable structure is prserved and peat results. The de-

[85] Travaux de la Société des Naturalistes de St. Petersbourg, 20; Annales Agronomiques, 17 : 17.

cay of humus is most rapid in drained and open soils. For this reason the presence of clay in a soil promotes the accumulation of humus. Inferior organisms are the means of diffusing oragnic matter through the soil. The mycelia of fungi grow on a dead root for instance, ramify laterally and thus carry organic matter outward and succeeding organisms extend this action and the soil becomes darkened in proportion. Humic acid in black soil is almost exclusively in combination with lime.

A more common view of the difference between the formation of humus above and below the water-level is that above the water-level there is a very free access of air and even the harder parts of the leaf skeleton can be oxidized through the agency of bacteria, while under the water-level there is a very limited supply of air and this oxidation cannot proceed as rapidly. The harder parts of the leaf skeleton are preserved, and from the freer access of air humus is oxidized more readily in drained and open soils, and accumulates in clay soils where there is less circulation of air.

The quantity of humus in the soils of arid regions is by no means so great as in those of abundant rain-fall. The influence of aridity on the formation of humus has been fully discussed by Hilgard.[86]

Few of the upland arid soils of the Pacific coast contain over .4% of humus, that is the "matiére noire" of Grandeau. This difference according to Hilgard is of importance because the humus of the soil is the chief repository of one of the most costly of the plant foods, *viz.*, nitrogen.

It must not be inferred however that such soils are very deficient in nitrogenous food since it appears that the humus of the arid soil has a higher percentage of nitrogen than that found in soils with abundant water supply.

The real composition of humus is a matter which has never been definitely determined. Composed as it is of many different but closely related substances it has been difficult to isolate and determine them.

[86] Report California Agricultural Experiment Station, 1892, 112.

The following table gives, according to the early views of agricultural chemistry, the composition of the bodies which form the larger part of humus:[37]

Ulmin and Ulmic Acid.		
Carbon.....	67.1 per cent.	Corresponding to $C_{40}H_{28}O_{12}+H_2O$.
Hydrogen.....	4.2 "	
Oxygen.....	28.7 "	
Humin and Humic Acid.		
Carbon.....	64.4 per cent.	Corresponding to $C_{40}H_{24}O_{12}+3H_2O$.
Hydrogen.....	4.3 "	
Oxygen.....	31.3 "	
Apocrenic Acid.		
Carbon.....	56.47 per cent.	Corresponding to $C_{24}H_{24}O_{12}+H_2O$.
Hydrogen....	2.75 "	
Oxygen.....	40.78 "	
Crenic acid.		
Carbon.....	45.70 per cent.	Corresponding to $C_{24}H_{24}O_{12}+3H_2O$.
Hydrogen.....	4.80 "	
Oxygen.....	49.50 "	

Aside from these humus compounds, there are others still less known and the action of which is not yet understood; among them are xylic acid, saccharic acid and glucinic acid, besides a brown humus acid containing carbon, 65.8 per cent., and hydrogen, 6.25 per cent., and a black humus acid yielding carbon, 71.5 per cent., and hydrogen, 5.8 per cent.

Berthelot and André ascribe to the insoluble form of humic acid the formula, $C_{18}H_{16}O_7$. This acid loses water slowly at ordinary temperatures and rapidly at 110° forming the insoluble anhydrid $C_{18}H_{14}O_6$. This acid and its anhydrid combine with potash and soda forming insoluble salts in which three atoms of hydrogen are replaced by the metal of the base.[38] It is evident that no serious attempt should be made to ascribe formulae to bodies of such a complex nature and variable composition.

The purest forms of these bodies have undoubtedly been made from sugar. The composition of ulmin and humin thus produced according to Mayer is as follows:

[37] Mulder: Chemie der Ackerkrume, 1 : 322; The Chemistry of Vegetable and Animal Physiology, Johnston's translation, 146 et seq.

[38] Beilstein's Handbuch der organischen Chemie, 3d edition, 1 : 1109.

	Ulmin.	Humin.
Carbon	63.4 per cent.	63.4 per cent.
Hydrogen	4.8 "	4.3 "
Oxygen	31.8 "	32.3 "

It is seen that there is but little difference in the composition of the two bodies.[39]

At the present time we can only regard the various forms of humus bodies as mixtures of many substances mostly of an acid nature and resulting from a gradual decomposition of organic matter under conditions which partially exclude free access of oxygen.

For analytical purposes it is important to separate these bodies by the best approved processes. A further knowledge of their composition can then be obtained by determining the percentages of carbon dioxid and water which they yield on combustion.

58. Artificial Humus.—The highly complex nature of natural humus excludes the possibility of ascribing to it a definite chemical formula. It is also believed in the present state of our knowledge that the bodies characterized by Mulder as humic and ulmic acids cannot be regarded as pure chemical compounds and that the isolation of such pure compounds has never been accomplished.

More reliable data are secured by converting definite compounds such as sugar and starch into a black organic substance of which the composition is more or less definite. This conversion takes place under the influence of heat and of acids or alkalies. Berthelot describes a process for converting sugar into a black substance by the action of hot hydrochloric acid.[40]

The substance thus formed, after the removal of all traces of the acid by prolonged washing in hot water, is brown-black, and amorphorus. Its centestimal composition is:—

C	66.41
H	4.57
O	29.02

[39] Mayer: Agrikulturchemie, 5th edition, 2 : first part. 76.
[40] Chemie Vegetale et Agricole, Paris, 1899, 4 : 123.

A product made from starch in a similar manner is composed of:—

C	65.7
H	5.0
O	29.3

From the above analysis the rational formula $C_{18}H_{14}O_6$ is proposed for this substance and with one molecule of water of hydration $C_{18}H_{16}O_7$.

These compounds resemble very nearly those prepared by Mulder when the differences in degree of desiccation and other changes in the environment of preparation are considered. This substance may be assumed to be humic acid.

59. **Salts of Humic Acid.**—Berthelot has prepared three potash salts from the humic acid above described, which have the following properties:

1. Monobasic salt which is insoluble and which is not broken up even under prolonged washing with water.

2. A tribasic salt which is insoluble but which is slowly decomposed in the cold under the influence of water until finally two-thirds of the alkali originally combined is extracted.

3. A polybasic salt containing a larger quantity of base than the foregoing and which is soluble in water.

It is concluded that humic acid is polybasic, losing a part of its water by simple desiccation and even in water at ordinary temperatures, thus undergoing a kind of dissociation. In this condition it unites with three equivalents of potash, forming insoluble salts. The first is monobasic, very stable and is formed with the evolution of + 18 Calories, practically the same as are produced by the formation of solid alkaline salts with strong mineral acids in a dilute state.

These humic substances like those of the soil, show also under the influence of a base, phenomena of hydration, and afterwards under the inverse action of an acid the effects of spontaneous dehydration by dissociation.

Humic acid is produced like sugars with absorption of heat; that is to say, it contains an excess of energy stored in its car-

bohydrates susceptible of being evolved by their total destruction.

60. Composition of Artificial Humus from Various Materials.— In order to compare humus substances of different origin Snyder has suggested a method of preparing them without the use of alkaline bodies.[41]

Various organic materials were mixed with a large excess of soil poor in humus and exposed to natural weathering for one year. For instance, 200 grams of sugar was mixed with 3000 grams of soil. Cow manure, green clover, meat scraps, wheat flour and old straw were among the materials used.

The humus materials produced from these various substances were obtained by extracting the soil, after treatment with dilute hydrochloric acid and distilled water, with a three per cent. potassium hydroxid solution. The alkaline humus extracts were neutralized with hydrochloric acid, which gave black and brown precipitates of humus materials, which were washed, dried, and prepared for analysis. The precipitated humus materials contained from 5 to 12 per cent. of ash, and had the following ultimate composition, on an ash-free basis:

	Humus Produced by						
	Cow manure. Per cent.	Green clover. Per cent.	Meat scraps. Per cent.	Wheat flour. Per cent.	Oat straw. Per cent.	Saw-dust. Per cent.	Sugar. Per cent.
Carbon.....	41.95	54.22	48.77	51.02	54.30	49.28	57.84
Hydrogen ...	6.26	3.40	4.30	3.82	2.48	3.33	3.04
Nitrogen	6.16	8.24	10.96	5.02	2.50	0.32	0.08
Oxygen	45.65	34.14	35.97	40.14	40.72	47.07	39.04
Total.....	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Highest. Per cent.		Lowest. Per cent.		Difference. Per cent.
Carbon.....	57.84	from sugar.	41.95	from cow manure.	15.89
Hydrogen ...	6.26	" cow manure	2.48	" oat straw	3.78
Nitrogen	10.96	" meat scraps	0.08	" sugar	10.88
Oxygen	47.07	" sawdust.	34.14	" green clover.	12.93

The differences in composition are noticeable. The humus produced by each material, as meat scraps, green clover, or sawdust, is different from the humus produced by every other mate-

[41] Journal of the American Chemical Society, 1897, **19** : 738

rial. There is not a general similarity in composition between the humus produced by any two of the materials. The humus produced by sugar may be taken as a type of a non-nitrogenous humus. The small amount of nitrogen present in the sugar humus has been derived from the nitrogen present in the soil. The humus from meat scraps may be taken as a type of humus produced from a nitrogenous material. The nitrogen content of the humus ranges from about 0.5 per cent. in sugar humus to nearly 11 per cent. in the meat scraps humus. The humus from such materials as meat scraps and green clover must be exceedingly complex, because each material is composed of both nitrogenous and non-nitrogenous compounds, and each class of compounds is capable of being split up into still other compounds, each one having a different action in humification processes. It is evident that any formulas applied to the compounds, as a whole, would, to say the least, fail to express the composition of humus.

Although the proximate composition of humus as yet, can not be given, or formulas assigned to these compounds, the nature of the humus as nitrogenous or non-nitrogenous can be determined.

It would seem best, in the present state of knowledge, to make the divisions on the basis of nitrogen, as:

I. The non-nitrogenous humus group, as sugar humus.

II. The nitrogenous group, divided into three or four subgroups, as (1) humus containing from one to two per cent. nitrogen, as sawdust humus; (2) humus containing from two to four per cent. nitrogen, as oat straw humus; (3) humus containing from four to eight per cent. nitrogen, as cow manure and clover humus; and (4) humus containing over eight or nine per cent. nitrogen, as meat scrap humus.

Such a division would give an approximate idea of the nature of the materials from which the humus has been derived, as well as indication of its agricultural value.

61. Influence of High Temperature on Humus.—The presence of an abundant supply of humus in a soil is usually regarded as an index of fertility, and in those soils which are deficient in humus, such as sandy and excessively clayey soils, the increase in humus content is an indispensable condition to the production of

permanent fertility. Large deposits of vegetable matter are therefore preserved from decay by cold weather.

The consumption of humus by the growing crop and by oxidation is very much more rapid at high than at low temperature.[42]

Boussingault pointed out more than 50 years ago that there were no peat-beds in the tropics except at a height of over 3000 feet on the plateaux of the Andes. The humus found in the soil of tropical forests is preserved by the thick vegetable cover and great humidity which prevent the development of a high temperature.

62. Functions of Humus.—Whether humus takes any direct part in the nutrition of green plants is not definitely known. De Saussure held that soluble humus was assimilated directly by vegetables and this is probably the case with those plants, such as mushrooms, which are devoid of chlorophyll.

Leibig held that humic acid is not absorbed by plants and that as such it does not form a part of their food. Humic acid being of a colloidal nature is not well suited to engage in the translations which takes place so readily with crystalline bodies in solution and which readily change their location under the stress of osmotic pressure.

Petermann found however that such bodies could be dialyzed in certain circumstances and he succeeded in passing through membranes highly nitrogenized organic matter of an amber color.[43]

The author found that sugar canes grown in peat soils contained a quantity of dark colored organic matter in their sap which persisted even in the raw sugar made therefrom.

He further found that the quantity of amid nitrogen in oats was greatly increased when grown on peaty soil.[44]

The chief functions of humus appear to be to modify the physical conditions of the soil with reference to texture, moisture, absorption of heat and mineral matters useful to plants and especially to hold in suitable form for progressive nitrification the partially decayed nitrogenous principles of vegetable matters.

[42] Breal: Annales Agronomiqnes, **20** : 353.

[43] Annales Agronomiqnes, **9** : 237.

[44] Wiley: Die landwirtschaftlichen Versuchs-Stationen, **49** : 193. Journal American Chemical Society, 1897, **19** : 605.

63. Soil and Subsoil.—Many subdivisions have been made of the above varieties of soil, but they have little value for analytical purposes. For convenience in description for agricultural purposes, the soil, however, is further divided into soil and subsoil. In this sense the soil comprises that portion of the surface of the ground, usually from four to nine inches deep, containing most of the organic remains of plants and animals and in which air circulates more or less freely for the proper humification of the organic matter, which usually gives a darker color to the soil than to the subsoil. The subsoil proper lies below this, and has usually more characteristic properties, especially in respect of color and texture, as it has been less influenced by artificial conditions of cultivation and the remains of vegetation.

The subsoil extends to an indefinite depth and is limited usually by deposits of undecomposed or partly decomposed rock matter, or by layers of clay, sand or gravel.

Inasmuch, however, as the influence of the subsoil on growing crops is of little importance below the depth of 18 inches the analysis of samples from a greater depth has more of a geological than agricultural value.

Hilgard regards as subsoil whatever lies beneath the line of change of color, or below the minimum depth of six inches. But should the change of color occur at a greater depth than 12 inches, the soil specimen should nevertheless be removed to the depth of 12 inches only, which is the limit of ordinary tillage; then another specimen from that depth down to the line of change, and then the subsoil specimens beneath that line. The depth to which the last should extend will depend upon circumstances. It is always desirable to know what constitutes the foundation of a soil to the depth of three feet at least, since the question of drainage, resistance to drought, etc., will depend essentially upon the nature of the substratum. But in ordinary cases 10 or 12 inches of subsoil will be sufficient. The sample should be secured in other respects precisely like that of the surface soil, while that of the material undelying this subsoil may be removed with less exactness, perhaps at some ditch or other easily accessible point, and should not be broken up like the other specimens.

In the method of soil sampling adopted by the Royal Agricul-

tural College of England, the soil is regarded as that portion of the surface of the ground which is reached by ordinary tillage operations, generally being from six to nine inches deep; the subsoil is that portion which is ordinarily not touched in plowing.

It is evident that no rigid definition of the difference between soil and subsoil can be made as the one gradually merges into the other. In general it may be said from the practical point of view that the soil is that part of the surface of the field extending to a depth of nine inches or to the depth turned by good plowing and the subsoil the layer of nine inches in depth immediately underneath the soil.

PART SECOND

SAMPLING SOILS FOR ANALYSIS

64. General Principles.—It would be unwise to attempt to give any single method of soil sampling as the only one to be practiced in all circumstances. In the methods which follow it is believed will be found directions for every probable case. The particular method to be followed will in each case have to be determined by circumstances.

The sole object in securing a sample of soil should be to have it representative of the type of soils to which it belongs. Every precaution should be observed to have each sample measure up to that standard.

The physical and chemical analyses of soils are long and tedious processes and are entirely too costly to be applied to samples which are not representative.

The particular place selected for getting the samples as well as the method employed are also largely determined by the point of view of the investigations. The collection of samples to illustrate the geological or mineralogical relations of soils is quite a different matter from gathering portions to represent their agricultural possibilities. In a given area the sum of plant food in the soil would only be determined by the analyses of samples from that particular field, while samples illustrating geological relations could or should be got at widely distant points. Again the chemist is content with a sample of a few hundred grams in weight while the physicist would require a much larger quantity. Much popular ignorance exists respecting the importance of the collection of soil samples. As an illustration of this may be cited a recent instance in which a sample of soil was received by the author with a request for a complete analysis and a statement of the kinds of crops it was suited to grow. No data relating to the locality from which the sample was taken accompanied this request. The sample itself, which weighed a little less than 3.6 grams, was not a soil at all in an agricultural sense but a highly ferruginous sand.

The collector of samples who understands the purpose for which he is working will find among the approved methods which follow some one or some combination of methods, by means of which his work can be made successful. In these cases it is the collector rather than the method on which reliance must be placed to secure properly representative samples.

65. General Directions for Sampling.—The locality having been selected which presents as nearly as possible the mean composition of the field a square hole is dug with a sharp spade to the depth of 18 inches. The walls of this hole should be smooth and perpendicular. The soil to the depth of from six to nine inches is then removed from the sides of the hole in a slice about four inches thick; or the sample of soil may extend to the depth indicated by a change of color. Any particles which fall into the bottom of the hole are carefully collected and added to the parts adhering to the spade. The whole is thrown into a suitable vessel for removal to the laboratory. The sample of soil having been thus secured, the subsoil is treated in the same way. It is evident also that the sample may be secured by removing the soil from the hole directly and then securing the sample of the subsoil. To insure uniformity in the samples, it is well to get several of them from the same field. Where more than one sample of the same type is collected it is advisable to mix all the sub-samples in the field, remove large sticks, stones, roots, etc., and select a general sample of from three to five kilograms. The characters and quantity of the débris removed should be carefully noted.

It is sometimes desirable to get samples of the subsoil to a greater depth than 18 inches. A post-hole auger or large wood auger will be found very useful for this purpose. It is rarely necessary to get samples of subsoil to a greater depth than six feet The geological formation and the general topography of the field should be noted, also the character of the previous crops, kind and amount of fertilizers employed, character of drainage and any other data of a nature to give a more accurate idea of the forces which have determined the physical and chemical properties of the sample. In case of a virgin soil the character of the natural vegetation is to be noted.

66. Method of Hilgard.—Hilgard recommends that samples

should not be obtained indiscriminately from any locality, but that consideration should be given to the chief varieties of soil which, with their inter-mixtures, make up the cultivable area of the region.[45]

As a rule, and whenever possible, samples should represent soils that have not been cultivated, or are otherwise likely to have been changed from their original condition of virgin soils and not ground frequently trodden over such as roadsides, cattle paths, or small pastures, squirrel holes, stumps, or even the foot of trees, or spots that have been washed by rains or streams, so as to have experienced a noticeable change, and not be a fair representative of their kind. The method proposed therefore is intended only for virgin soils. He further suggests that the normal vegetation, trees, herbs, grass, etc., should be carefully observed and recorded, and spots showing unusual growth whether in kind or quality be avoided as such are likely to have received some animal manure or other addition.

Specimens should be secured from more than one spot judged to be a fair representative of the soil intended to be examined as an additional guarantee of a fair average.

After selecting a proper spot pull up the plants growing on it, and scrape off the surface lightly with a sharp tool to remove half-decayed vegetable matter not forming part of the soil. Dig a vertical hole, like a post-hole, at least 20 inches deep. Scrape the sides clean so as to see at what depth the change of tint occurs which marks the downward limit of the surface soil, and record it. Remove at least half a bushel of the earth above this limit, and on a cloth (jute bagging should not be used for this purpose, as its fibers, etc., become intermixed with the soil) or paper break it up and mix thoroughly, and put up at least a pint of it in a sack or package for examination. This specimen will, ordinarily, constitute the soil. Should the change of color occur at a less depth than six inches the fact should be noted, but the specimen removed to that depth nevertheless, since it is at least a depth to which rational cultures can be supposed to reach.

In case the difference in the character of a shallow surface soil

[45] Bulletin 68 Division of Chemistry, 60 et seq.; Tenth Census, 1880, 5 : 67 et seq.

and its subsoil should be unusually great, as may be the case in tule or other alluvial lands or in rocky districts, a separate sample of that surface soil should be got, besides the one to the depth of six inches.

Specimens of salty or alkali soils should, as a rule, be secured only toward the end of the dry season, when they will contain the maximum amount of the injurious ingredients which it may be necessary to neutralize.

Whatever lies beneath the line of change, or below the minimum depth of six inches, will constitute the subsoil. Should the change of color occur at a greater depth than twelve inches the soil specimen should nevertheless be obtained to the depth of twelve inches only, which is the limit of ordinary tillage; then another specimen from that depth down to the line of change, and then the subsoil specimen beneath that line.

Hilgard justly calls attention to the fact that all peculiarities of the soil and subsoil, their behavior in wet and dry seasons, their location, position and every circumstance in fact, which can throw any light on their agricultural qualities or peculiarities should be carefully noted and the notes sent with the samples. Unless accompanied by such information, samples can not ordinarily be considered as justifying the amount of labor involved in their examination. When the sample is not to be used immediately it should be air-dried as soon as possible. Otherwise the activity of the organisms it contains will continue and profound changes in composition may ensue, especially in the nitrogenous matters which may be present.

When available the geological maps of the region where samples are secured should be consulted in order that the information respecting the origin of the soil may be utilized.

The kind of analyses to which a sample is to be subjected also largely determines the method to be pursued in selecting it: For instance, a sample to be used for determining the size of the particles therein, may be obtained in quite a different manner from that designed only for the determination of moisture, or for partial or complete physical and chemical analysis.

67. In the directions collated by Richards and which have been largely followed by the correspondents of the Department of Ag-

riculture, it is recommended to select in a field, four or five places, at least, per acre, taking care that these places have an homogeneous aspect, and represent as far as possible the general character of the whole ground.[46] If the field, however, present notable differences, either in regard to its aspect or its fertility, the samples gathered from the different parts must be kept separate.

The sampling of arable soil should be made only after the raising of the crop and before it has received any new manure. In other soils the sample should represent only spots that have not been cultivated.

68. **Caldwell** advises that according to the purpose of the analysis samples be secured:[47]

a, from one or from several spots in the field, in order to subject each sample to a separate analysis; or

b, for an average representation of the soil of the whole field; in this case, several portions of earth are gathered from points distributed in a regular manner over the field, all of which are most carefully mixed together, and from four to six kilograms of the mixture, free from any large stones, are preserved as the average sample.

An excavation in the soil from 30 to 50 centimeters deep, or through to the subsoil, and from 30 to 50 centimeters square, with one side as nearly vertical as possible is made and a slice taken from this side of uniform thickness throughout, weighing from four to six kilograms. If the subsoil is to be examined, a sample of it should be removed in the same manner as directed for the upper soil, to the depth of about 20 centimeters.

If the character of the soil varies materially in different parts of the field, samples from several spots should be analyzed separately.

A small portion of the sample should be put at once in a well-stoppered bottle; the remainder may be allowed to become air-dried, by exposing it in a thin layer, in summer, to the common temperature in the shade, or, in winter, to that of a warm room, or a moderately warm drying-chamber, heated to 30°-40°; in either case it should be carefully protected from dust.

[46] Bulletin 10 Division of Chemistry, 33.

[47] Caldwell's Agricultural Analysis, 166.

At the time of getting the sample of the soil, observations should be made in regard to the following points:

a. The geognostic origin of the soil.

b. The nature of the underlying strata, to the depth of from one to two meters, if practicable.

c. The meteorology of the locality, by consulting meteorological records, if possible; otherwise, by the general opinion of the neighborhood; in this connection, the height of the locality above the level of the sea should be noted also.

d. The management and rotation of crops in previous years.

e. The character of the customary manuring.

f. The amount of the crops removed in the preceding year, and, if possible, the average amount of each of the more important crops yielded by the field.

g. The practical judgement of neighboring farmers in regard to the field.

Caldwell's method is practically identical with that of Wolff which was one of the earliest of the systematic schemes for getting soil samples.[48]

69. **Method of the Official Agricultural Chemists.**[49]—Surface accumulations of decaying leaves, etc., are removed and a slice of uniform thickness from the surface to the desired depth secured. To eliminate the effects of accidental variations in the soil, select specimens from five or six places in the field and remove several pounds of the soil, to the depth of six inches, or to the change between the surface soil and the subsoil, in case such change occurs between the depth of 6 and 12 inches. In no case is the sample to be got to a greater depth than 12 inches. If the surface soil extend to a greater depth, a separate sample below the depth of 12 inches is to be obtained. If the surface soil extend to a depth of less than six inches, and the difference between it and the subsoil is unusually great, a separate sample of the surface soil is secured, besides the one to the depth of six inches.

The depth to which the sample of subsoil is secured will depend on circumstances. It is always necessary to know what

[48] Zeitschrift für analytische Chemie, **3** : 87.

[49] Bulletin 46 Bureau of Chemistry, 71.

constitutes the foundation of a soil, to the depth of 3 feet at least, since the question of drainage, resistance to drought, etc., will depend essentially upon the nature of the substratum. But in ordinary cases 10 or 12 inches of subsoil will be sufficient for the purposes of examination in the laboratory. The specimen is obtained in other respects precisely like that of the surface soil, while that of the material underlying this subsoil may be removed with less exactness, perhaps at some ditch or other easily accessible point, and should not be broken up, but left, as nearly as possible, in its original state. Mix these soils intimately, remove any stones, shake out all roots and foreign matters, expose in thin layers in a warm room till thoroughly air-dry, or dry in an air-bath at a temperature of not above 40°.

The soil is rapidly dried to arrest nitrification. It is not heated above 40° lest there be dissipation of ammonium compounds, or a change in the solubility of the soil. The normal limit to which the soil may be heated in place by the sun's rays should not be exceeded in preparing a soil for an agricultural chemical analysis.

Five hundred grams or more of the air-dried soil, which may be either the original soil or that which has been passed through a sieve of coarser mesh, are sifted through a sieve with circular openings one-half millimeter in diameter, rubbing, if necessary, with a rubber pestle in a mortar until the fine earth has been separated as completely as possible from the particles that are too coarse to pass the sieve. The fine earth is thoroughly mixed and preserved in a tightly stoppered bottle, from which the portions for analysis are weighed.

The coarse part is weighed and examined microscopically or with Thoulet's solution described in part fifth.

70. **Method of the Official French Commission.**—The official French commission emphasizes the fact that the sample of soil used for analysis, should represent a layer of equal thickness through the total depth of its arable part.[50] An analysis of the subsoil secured in the same way, will often be useful to complete the data of the soil study.

[50] Annales de la science agronomique, 8th year, 1 : 240, et seq. The commissioners were Messrs. Risler, Grandeau, Joulie, Schloesing and Müntz.

First of all, according to this authority, it is necessary to determine the point of view from which the sample is to be obtained. If the object is a general study, having for its aim the determination of the general composition of the soils of a definite geological formation, the sample should be of such a nature that the different characteristics of the soil alone should enter into consideration without paying any attention to its accidental components, which have been determined by local causes, such as are produced by continued high cultivation, the application of abundant fertilizers, or the practice of a particular line of agricultural industry. The samples of soil therefore, with such an object in view, should represent parts of the earth which are beyond the reach of the causes mentioned above and which tend to modify the nature of the primitive soil. In such a case it is the soil which has not been modified, or better still, virgin soil, such as is found in the woodlands and prairies, which should be used for a sample, choosing those places in which the geological formation is most perfectly characterized. In such a case a sample from one spot corresponding to the conditions before mentioned, would be the best for the purposes in view. The sample would thus represent a true type to be studied, not one of a mean composition got by sampling from different localities and mixing them into a homogeneous parcel. This last method of proceeding may introduce into the sample earth modified by culture or by influences purely accidental. However, it would be wise, in a region characterized by the same geological formation, to secure a certain number of samples in different localities, and examine singly each one of them in order to be assured that there is a uniformity of composition in the whole of the soils.

If, on the contrary, it is the purpose of the investigation to furnish information to the cultivator concerning the fields which are worked, it is necessary to approach the problem from a different point of view. In this case the earth which is under cultivation should be first of all considered with all the modifications which nature causes or practical culture has caused in it. But it often happens that upon the same farm the natural soil is variable, caused either by the washings from the adjacent soils, by the ac-

cumulation at certain points of deposits formed from standing water, or from other reasons. In such a case it would be necessary to get samples from every part of the field which exhibited any variation from the general type, in order to get a complete mean sample of the whole. It is necessary to be on guard against making a mixture of these different lots which would neither represent the different soils constituting the farm nor their mean composition. It would be better to examine each of these samples alone and then from those parts which appear to have a similar composition, to get a general sample for the mean analysis.

Most often it is necessary to confine our studies to the really important part of the farm the composition of which would have a practical interest. The aspect of the spontaneous vegetation in such a case, will often serve as a guide to determine the parts of the farms which are similar in nature. The sample should represent the arable layer, properly so-called, that is, that part of it which is stirred by the agricultural implements in use and in which the root system of the plant takes its greatest development and which is the true reservoir of the fertilizing materials.

When a trench is dug in the soil it is easy to distinguish the arable layer from the subsoil. In the first place, its color is different, generally being modified by vegetable débris which forms the supply of humus. The depth of the arable layer is variable, but it is most frequently between 200 and 300 millimeters. In the analysis the depth and layers should be indicated since the chemical composition of the earth varies according as the sample is taken to a greater or less depth. As an example of this it may be said that the quantity of nitrogen decreases in general in proportion as the depth of the layer is increased. The sample therefore, should be limited exactly to the arable layer of soil.

The latest directions for soil sampling according to the accepted French methods are described by Deherain.[51]

Since the sampling is the first step in the study of the soil in the laboratory it is highly important that it be properly done. If the field be a large one the surface as a whole should first be carefully examined to determine the degree of homogeneity. If this first view shows the presence of different types of soils as many

[51] Traité de Chimie Agricole, 1902 edition, 396.

samples as there are different types should be secured. The samples are then to be secured with a spade as already described. At Grignon the samples are obtained from eight different places. The subsamples thus secured are thoroughly mixed and reduced by continued division to the quantity required. If the object be to determine the moisture in the sample it is spread out on paper, mixed by hand, the pebbles removed and 20 grams of the fine earth placed in the oven and dried for 10 or 12 hours.

The rest of the sample left to air dry for some days if too wet serves to form masses of from one to one and a half kilograms reserved for analysis.

In sampling it is necessary to remove from the surface the living and dead vegetation which covers the soil. With a spade a square hole is then dug to the depth of about 500 millimeters; in other words, to a depth considerably exceeding that of the arable layer. Afterwards on each of the four sides of the hole there is removed by the spade, a prismatic layer of the arable portion of a thickness equal to its depth. The samples thus obtained are united together and carefully mixed for the purpose of forming a sample for analysis. If there are large stones they are removed by hand and their proportion by weight determined.

In all cases it would prove useful to get a sample of the subsoil which is far from playing a secondary rôle. The rootlets bury themselves deeply in it and seek there a part of their nourishment. The subsoil, therefore, furnishes an important addition to the alimentation of the plants. For sampling the subsoil a ditch is dug of sufficient depth, say one meter, and the arable soil carefully removed from the top portion. Afterwards pieces are taken from the four sides of the hole at variable depths, which should always be indicated, and which should extend in general, from six to eight-tenths of a meter below the arable soil since it is demonstrated that the roots of nearly all plants go at least to this depth. The analysis of the subsoil, however, is less important than that of the soil, properly so-called, because the agronomist does not act directly upon it and takes no thought of modifying it and enriching it as he does the layer of arable soil. But the composition of the subsoil is a source of information capable of explaining certain cultural results and capable sometimes, of lead-

ing to the correct way of improving the soil, as in cases where the subsoil can be advantageously mixed with the superficial layer.

71. **In** the method of soil sampling adopted by the German Experiment Stations it is directed that the samples of soil should be secured according to the extent of the surface to be sampled, in 3, 5, 9, 12 or more places at equal distances from each other.[52] They should be cut in perdendicular sections to the depth turned by the plow; and for studies of the subsoil to a depth of from 60 to 90 centimeters. The single samples can be either examined separately or carefully mixed and a suitable portion of the mixture transfer to this place.

The directions given by König for soil sampling are those prescribed by the Association of Agricultural Experiment Stations of the German Empire.[53] He adds that the different samples should be mixed together only when they are practically alike as determined by outward appearance or by testing for carbonate of lime with hydrochloric acid. If the several portions of the soil removed develop any peculiarities separate samples should be made of all those displaying like characterics. Instead of a spade, an auger or American post-hole auger may be used.

72. **Wahnschaffe** insists on rather a fuller preliminary statement to accompany soil samples but gives essentially the method of Wolff with some unimportant variations which add little to the value of the process.[54]

73. **Method of Peligot.**—The getting samples of soil of which the physical and chemical properties are to be determined is a delicate operation.[55] These samples should represent as nearly as possible the mean of both the good and bad qualities of a soil.

In the field selected are chosen a certain number of places at least four or five per hectare. The spots selected should have a homogeneous appearance resembling as nearly as possible the general aspect of the field.

[52] Die landwirtschaftlichen Versuchs-Stationen, **88** : 291 and 309.

[53] Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, 2nd edition, 4.

[54] Anleitung zur wissenschaftlichen Bodenuntersuchung, 17.

[55] Traité de Chimie analytique appliqué á l'Agriculture, 1883, 149.

By means of a spade a few kilograms of earth are removed to the depth of the subsoil being careful to include in the sample no accidental detritus which the upper part of the soil especially may contain. The samples should be secured immediately after the crop is harvested and before any fresh fertilizer is applied. The samples are carefully mixed and placed in a glass bottle or flask.

The sample of subsoil is obtained in the same manner. If the field presents notable differences in appearance or fertility all the samples should be examined separately.

74. **Sampling with an Auger.**—When small samples only are required for partial or preliminary study they are conveniently secured by the method recommended by Whitney.[56]

An ordinary wood auger, two and one-half inches in diameter is so arranged as to admit of additions to the stem to enable the operator to get samples at different depths. It may be fitted with a short piece of gas pipe for a handle and the several pieces of which it is composed may be taken apart and carried in a knapsack.

In sampling the boring is continued until a change in color shows that the subsoil has been reached. The auger cuts a very clean sample save in excessively sandy soil. After the soil sample is secured the hole is cleaned out and the sample of subsoil removed by the same instrument. In sampling heavy soils the auger should be removed at least once for each depth of six inches.

It is evident that the auger could not be used to advantage in sampling gravelly soils. The soil is conveniently preserved in heavy cloth bags of which the usual size is six by eight and one-half inches. Where larger samples are required the size of the bag is correspondingly increased. Each bag is to be tagged or labeled to correspond with the entry in the note book.

Samples to determine the amount of empty space in a soil are secured as follows: The sampler is a piece of brass cylinder about nine inches long and one and a half inches in diameter. A piece of clock spring is soldered in one end and sharpened to give a good cutting edge. This arrangement permits the sample to pass into the cylinder without much friction. The area enclosed by the clock spring is accurately determined and a mark is placed in the cylinder six inches from the cutting edge. The apparatus is driven

[56] Bulletin 35 Division of Chemistry, 108.

into the soil to a depth of six inches, a steel cap being used to prevent the hammer from injuring the cylinder. The earth is next removed from about the cylinder with a trowel, and the separated earth is cut smoothly off by a sharp knife and removed together with its brass envelope. The sample is taken to the laboratory in a cloth bag, dried and weighed. The specific gravity of the sample is determined and the volume occupied by a given amount calculated.

75. **Sampling for Moisture Determination.**—In the method of Whitney a number of brass tubes is provided 9 inches long and ¾ inch in diameter and with a mark 6 inches from the bottom.

The tube is pushed down into the soil to the mark and the sample of soil removed with the tube. There is but little danger of the sample dropping out of the tube even in sandy soils. When the tube is withdrawn each end is capped with a rubber finger tip making a perfectly air tight joint. The tubes containing the samples can be kept several days with no fear of losing moisture. This method is especially useful in getting samples from observers in different localities who can enclose the tubes in a cloth sack and send them to the laboratory by mail daily or at stated intervals. A tube of the size given holds about fifty grams of soil.

76. **Sampling to Determine the Permeability of Soil to Water or Air.**—Whitney determines the permeability of soil or subsoil to water or air in the following manner:[57]

An excavation two feet square and 18 inches deep is made in the soil. On one side of this hole the sample of soil or subsoil is secured by means of a narrow saw blade and a sharp carving knife. The sample of soil should be two inches square and from three and a half to four inches long. It is placed in a brass cylinder three inches long and three and a quarter inches in diameter. The open space in the cylinder is filled wtih paraffin heated just to its melting point. As the paraffin cools the upper surface should be kept stirred to prevent the mass when set from receding from the square column of soil. Care must be taken to keep the paraffin from the ends of the soil columns and these should be left, as far as possible in their natural condition.

The rate of percolation of the water may be determined at the

[57] Bulletin 35 Division of Chemistry, 111.

time the sample is secured. For this purpose an additional section of brass tube two inches long is fastened to the one holding the sample by a rubber band. An iron rod is driven into the earth carrying a retort stand ring supporting a funnel filled with fine gravel. The lower end of the soil column in the brass cylinder is placed on this gravel. Water is next carefully poured upon the top of the sample of soil being careful not to disturb the surface. The surface of the sample may be protected with a little fine sand. The water may be poured on the paraffin thus affording an additional protection to the soil surface. When the water begins to drop from the funnel a graduated glass is set under it and the time required for a given volume to pass through under an initial pressure of two inches is noted. The volume required represents one inch in depth over the four square inches of soil surface, *viz.:* four cubic inches.

77. **Method of the Royal Agricultural Society.**[58]—Have a wooden box made, 6 inches long and wide, and from 9 to 12 inches deep, according to the depth of soil and subsoil in the field. At one of the selected places mark out a space of 12 inches square; dig around it in a slanting direction a trench, so as to leave undisturbed a block of soil, with its subsoil, from 9 to 12 inches deep; trim this block to make it fit into the wooden box, invert the open box over it, press down firmly, then pass a spade under the box and lift it up and gently turn it over.

In the case of very light, sandy, and porous soils, the wooden box may be at once inverted over the soil and forced down by pressure, and then dug out.

Proceed in the same way for collecting the samples from all the selected places in the field, taking care that the subsoil is not mixed with the surface soil. The former should be sampled separately.

In preparing the plot for the gathering of the sample, take care to have it lightly scraped so as to remove any débris which may be accidentally found there.

The different samples thus procured are emptied on a clean, boarded surface, and thoroughly mixed, so as to incorporate the different samples of the same field together. The heap is then

[58] Bulletin 10, Division of Chemistry, 33.

divided into four divisions, and the opposite quarters are put aside, taking care to leave the two remaining ones undisturbed; these are thoroughly mixed together, the heap divided into quarters, and the opposite ones taken away as before. This operation of mixing, dividing into quarters and taking away the opposite quarter is continued until a sample is left weighing about 10 or 12 pounds.

Thus is obtained the average sample of the soil. Of course where only a single sample is desired from the field this method of quartering is not resorted to, but the bottom of the box is nailed directly on and sent to the laboratory, where the soil is to be analyzed. The above method has been modified by Lawes as follows:

78. **Method of Lawes.**—In the method of sampling proposed by Lawes a steel frame 10 by 12 inches, and nine inches deep open at top and bottom is driven into the earth until its upper edge is level with the surface of the soil.[59] All above-ground vegetation is then cut off as closely as possible with scissors. The soil within the frame is then removed exactly to the depth of the frame, and immediately weighed. It is then partially dried, and mechanically separated by a series of sieves, all visible vegetable matter being at the same time picked out. The stones and roots and the remaining soil are thus separated, and the determinations of dry matter, nitrogen, etc., are made in the separated soil after being finely powdered. The loss of water at each stage of preparation and on drying the samples as analyzed is also carefully determined. This method which requires the soil to be gathered to an arbitrary depth of nine inches, could not be used when samples of strictly arable soil are to be studied.

79. **Method of Warrington.**—Dyer at the suggestion of Lawes and Gilbert recommends the general adoption of the Rothamstead method of sampling described by Warrington.[60]

This method is an amplification of that just described.

A frame made of stout sheet iron, in shape a rectangular prism open at top and bottom, is driven into the soil by repeated blows

[59] Journal of the Royal Agricultural Society, [2] **25** : 12.

[60] Bulletin 62, Division of Chemistry, 86; Office of Experiment Stations, 1892, Bulletin 8, 39.

of a wooden rammer till the soil has the same level inside and outside the frame. The soil inside the frame is then cut out and constitutes the sample of the first depth, or surface soil. That the frame is accurately emptied is ascertained by trials with a wooden gauge of the same depth as the iron frame. If a sample of the next depth is desired the soil is cleared away around the outside of the frame till the level is reduced to that of the bottom of the frame; the frame is driven down again and the former operations are repeated.

Soil sampling at Rothamsted is usually carried down to three depths, but in a good many cases it has been carried down to 12 depths. The area of the sampling frame used for the first depth is usually 144 square inches (12 by 12 inches) a smaller frame (six by six inches) being used for the succeeding depths.

The iron frame has a stout rim along its upper edge to increase its strength. The best sampling frame is made of cast steel; this form of frame needs no rim.

When the soil sampling is carried below the first depth care must be taken when digging around the frame that each depth of soil removed is placed by itself, so that when the pit is filled in the soil may be returned to its proper position. A record must be kept of the place where the sampling is conducted, as a soil can not be accurately sampled twice in the same place.

Each sample of soil is weighed as soon as it is removed from the frame, and is put into a bag by itself. When the soil reaches the laboratory it is at once broken up by hand into small pieces, and laid on paper trays, which are placed on the shelves of a storeroom kept at a temperature of about 55° till thoroughly dry; each sample is then returned to its bag. This immediately drying the soil at a low temperature is essential if changes in the organic matter, and especially nitrification, are to be stopped. This practice dates at Rothamstead from 1877. After drying the soil it may be stored till leisure is found for further work. Each bag is then weighed. The soil is crushed and passed through a ¼ inch sieve; the stones that do not pass through this sieve are weighed. All that passes through the sieve is thoroughly mixed and a sufficient quantity is finely powdered for analysis. Mixed samples are

prepared after the soil has passed through the ¼ inch sieve or after it has reached the stage of fine powder.

80. **Grandeau** recommends without change the methods of soil sampling adopted by the Eastern Agricultural Station of France.[61] In sampling soils there are two cases to be considered; first a homogeneous soil and second, a soil variable in its appearance and composition. First, if the soil is homogeneous, being of the same geological formation it will be sufficient to get a mean sample in accordance with the following directions:

The field is first divided by diagonals or by transverse lines the direction of which need not be fixed in advance but as inspection of the form and configuration of the field may indicate. In the ordinary conditions of homogeneity (marly, granitic, argillaceous or silicious soils) it will be sufficient to select about five points per hectare from which the samples are to be taken. These points having been determined the surface is cleaned in such a way as to remove from it the detritus which may accidentally cover it; such as dry leaves, fragments of wood, foreign bodies, etc. The surface having been prepared, (five-tenths to six-tenths square meter) a hole is dug four-tenths of a meter long and as wide as the spade employed. The sides should be as nearly vertical as possible. As to depth it varies with the usage of the country in regard to tillage. The layer of arable earth is what in effect properly constitutes the soil. It ought not to be mixed with any fragments of the subsoil. When the hole is properly cleaned the samples are secured with a spade from the sides of the excavations. About five kilograms are sufficient. The soil is placed in a proper receptacle as it is removed from the hole.

This operation is repeated on as many points as may be necessary to obtain a mean sample of the soil of the whole field.

All the samples are now collected on a table sufficiently large, and intimately mixed together. Two samples, each of about five kilograms, are then made from the mixed material. One sample is immediately placed in bottles and carefully stoppered and sealed; the other is dried in the sun or on the hearth of a furnace. When sufficiently dry the second sample is also placed in bottles and well stoppered. While mixing the samples, pebbles, etc., of

[61] Traité d'Analyse des Matiéres Agricoles, 3d edition, 1897, 1 : 131.

the size of a nut and larger are removed, the weight of the rejected matter being determined. The nature of the pebbles should also be noted; whether silicates, limestone, etc.

The sample of subsoil is secured in exactly the same manner, using the same holes from which the samples of soil were removed. The nature, the aspect and the order of the strata will indicate the depth to which the subsoil should be sampled. In general, a depth equal to that of the sample of soil will be sufficient. The depth to which the roots of cultivated plants reach is also a good indication in selecting a sample of the subsoil. In forests the sample of subsoil should be obtained from four to five-tenths of a meter below the plane where the horizontal roots lie.

If the soil in respect of its geological formation, its fertility or its physical aspect presents great differences, special samples should represent each part in accordance with the directions given above.

81. **Wolff** suggests that a hole 30 centimeters square be dug perpendicularly and a section from one of the sides removed for the sample generally to the depth of 30 centimeters the sample shall be regarded as soil and to the additional depth of 30 centimeters as subsoil.[62] Local conditions may require a proper variation from these dimensions. The thickness of the section may vary according to the quantity of the sample desired. For analytical purposes, five kilograms will usually be sufficient. When culture experiments are also contemplated a larger quantity will be required. Further suggestions in regard to sampling are found in the directions already given from Caldwell.

82. **Method of Wahnschaffe.**—The method of sampling advised by Wahnschaffe is but little different from that of Wolff already mentioned.[63]

With a spade a square sample hole is dug having its sides perpendicular to the horizon. The soil which is removed is thrown on a cloth and carefully mixed. From the whole mass a convenient amount is next removed care being taken not to include any roots. In a similar manner it is directed to proceed for the sample of subsoil. At first the subsoil should be removed to a depth

[62] Zeitschrift für analytische Chemie, 8 : 87.

[63] Anleitung zur wissenschaftlichen Bodenuntersuchung, 2nd edition.

of two or three decimeters. The number and depth of subsequent samples will depend chiefly upon the character of the soil. Where sampling extends to the depth of two meters the use of a post-hole auger is recommended.

The samples should not be too small. In general from two to three kilograms should remain after all preliminary sampling is finished.

83. **Instruments Employed in Sampling.**—In general a sharp spade or post-hole auger is quite sufficient for all ordinary sampling but for certain special purposes other apparatus may be used.

The instrument which is used by King consists of a thin metal tube of a size and length suited to the special object in view, provided with a point which enables it to cut a core of soil smaller than the internal bore of the tube and at the same time make a hole in the ground larger than its outside diameter.[64] Its construction is shown in figure 9, in which A B represents a soil tube in-

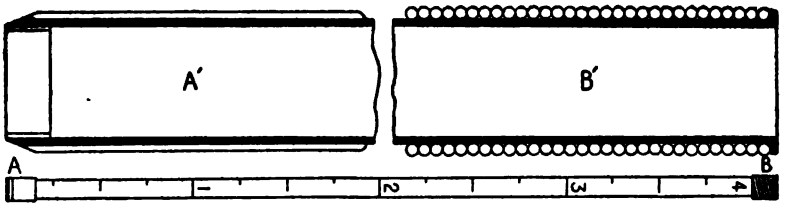


Fig. 9.

tended to get samples down to a depth of four feet. A′ is an enlarged cross-section of the cutting end of the tube, which is made by soldering a heavy tin collar, about three inches wide, to the outside of a large tube allowing its lower end to project about one-half an inch. Into this collar a second one is soldered with one edge projecting about one-quarter of an inch and the other abutting directly against the end of the soil tube. Still inside of this collar is a third about one-half an inch wide which projects beyond the second and forms the cutting edge of the instrument.

The construction of the enlarged head of the tube is shown at B′. It is formed by turning a flange on the upper end of the tube and then wrapping it closely with thick wire for a distance of

[64] Seventh Annual Report Wisconsin Experiment Station, 161.

about three inches, the wire being securely fixed by soldering. The soil tube should be as light as possible not to buckle when being forced into the ground, and the cutting edge thin. The brass tubing used by gas fitters in covering their pipes has been found very satisfactory for ordinary sampling. With a one inch soil tube four feet long it is possible to get a clear continuous sample of soil to that depth by simply forcing the tube into the ground with the hand and withdrawing it, or the sample may be had in sections of any intermediate length. Later in the season when the soil becomes dryer it is necessary to use a heavy wooden mallet to force the tube, and this should be done with light blows.

The closeness with which it is possible to duplicate the samples in weight by this method will be seen below, where from each of four localities three samples were secured from the surface to a depth of four feet.

SHOWING VARIATIONS IN THE DRY WEIGHT OF TRIPLICATE SAMPLES OF SOIL

	A.	B.	C.
I. Surface to four feet.....	716.6 gms.	715.5 gms.	710.3 gms.
II. Surface to four feet.....	715.4 gms.	687.1 gms.	731.2 gms.
III. Surface to four feet.....	654.0 gms.	688.3 gms.	709.0 gms.
IV. Surface to four feet.....	714.0 gms.	687.8 gms.	719.3 gms.

These four series of samples were got at the four corners of a square 12 feet on a side and serve to show how much samples may vary in that distance. The large difference shown in III, A is due to the fact that the soil tube penetrated a hole left by the decay of a rather large root as shown by the bark in the sample. When it is desired to determine accurately the dry weight of the soil per volume the cutting joint of the tube should be made of tool steel, bored accurately to a standard diameter and tempered.

84. Auger for Sampling.—It has already been said that the ordinary auger used for boring fence post-holes may be used to advantage in sampling soil. Large wood augers can also be used to advantage for the same purpose. For special purposes, however, other forms of augers may be used.

Norwacki and Borchardt have described a new auger for sampling soil for analytical purposes.[65]

In figure 12, A, B and C show the general exterior and interior form of the instrument. The handle is hollow and made of iron gas pipe covered with leather. On the inside of this, in the mid-

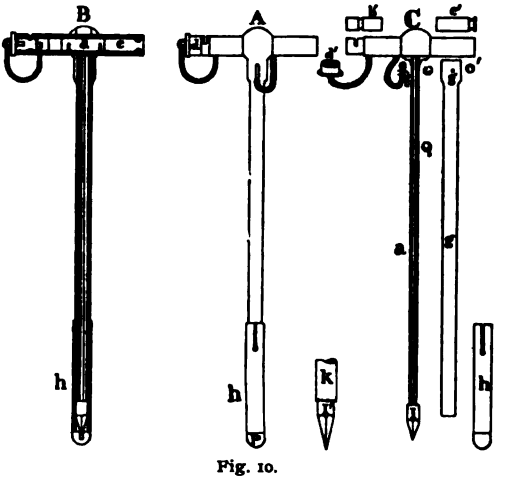


Fig. 10.

dle, is fixed a wooden plug a, which leaves two compartments, one in each end for holding the brass plug b′, and the wicker lubricating wad c′. The stem of the auger a, is heavy and made of eight-sided steel and the under end is strengthened with a heavy casting fitting into the auger guide g g. The end of the auger I I′ is triangular and hardened. The auger guide g g, is made out of a single piece of drawn steel tubing. Above it is strengthened by a ring-shaped piece of iron or copper and its lower end is furnished with saw teeth as shown in K and is hardened . The fixing key e, is bent in the form of a hook and can be passed through the two holes o o, of the auger stem and through the one hole o′ in the strengthened part of the auger guide. It permits the auger guide to be fixed upon the auger stem in two different positions, higher and lower. On one end it is cut squarely across and on the other provided with a conical hole drilled into it. It fits on the one hand exactly in the auger guide and on the other loosely plays in the

[65] Deutsche landwirtschaftliche Presse, 19, No. 35, 383-4.

cavity of the handle at b, designed to hold it when not in use. The cap d′ is made of heavy sheet brass and is fastened upon the end of the handle after the manner of a bayonet. The wicker cartridge is made of rolled and sewed wicker-work. At the upper end it is provided with a metallic button and before use it is saturated with paraffin oil. It fits on the one side firmly in the auger guide and on the other in the cavity of the handle c where it is kept when not in use. The union h is made of a brass tube which below is closed with a piece of solid brass upon the inside of which a hole is bored. In this hole rests the end of the auger stem when the union is placed firmly upon the auger guide.

The auger is placed together as is shown in A B, the union h is taken off and it is driven with gentle blows, turning it back and forth, to the proper depth into the soil. After the key is loosened the auger is lifted high enough so that the second hole appears and then it is fixed in position by the key. Then the boring is continued, turning the auger to the right, by which the auger, eating its way with its saw teeth, presses deeper into the ground and withdraws the material for analysis. After the auger guide has been filled through any desired length, say from five to ten centimeters with the sample of soil, the whole auger is drawn out of the soil, the key removed, the auger stem withdrawn from the auger guide, the apparatus opened by turning the bayonet fastening of the stopper on the handle, the brass plug placed in the end and then with the smooth part forward, from above, it is allowed to fall into the auger guide until it reaches the soil. The auger stem is then put back, the point of it fitting into the hole of the plug and the sample of soil shoved out of the auger guide. The auger guide is again fixed on the auger stem by the key and then the apparatus is ready for a second operation. When the borings cease the wicker cartridge is drawn out of the handle and shoved, the soft end forward, from above, into the auger guide and the brass plug after it and pushed through with the auger stem. By this process the wicker cartridge gives up a sufficient amount of paraffin oil to completely grease the inside of the auger guide and to protect it from rust. After use the instrument should be cleaned on the outside by means of a cloth, the plug and wicker wad replaced in

their proper positions, the cap fixed on the handle and the union on the point of the instrument.

The length of the whole apparatus may reach one meter or more; the internal diameter 16 millimeters. The apparatus weighs with a length of one meter, together with all its belongings, about two kilograms. For the investigation of peat and muck soils as well as sand, instead of the steel auger guide one of brass or copper can be used. For this purpose the length of the apparatus may reach three or four meters.

In comparison with other apparatus which are used for sampling, it appears without doubt that with the one just described a better and less mixed portion of the soil can be obtained at great depths. The apparatus is said to have many advantages over a similar one known as Fraenkel's, and is much more easy to clean. The advantages of the apparatus are said to be the following: The farmer with this piece of apparatus in a short time can go over his whole farm sampling to the depth of 90 centimeters since a single boring does not take more than one minute. Geologists and others interested in the soil at greater depths can use an apparatus from three to four meters in length and obtain unmixed samples from these lower depths. These are also interesting from a bacteriologic point of view. The entire apparatus is especially valuable for the investigation of the lower parts of peat and muck soils. The apparatus has been tried in the collection of samples for the laboratory of the Department of Agriculture but it is too complicated to be recommended for ordinary use. When however samples are required from considerable depths as in peaty soils it is highly satisfactory.

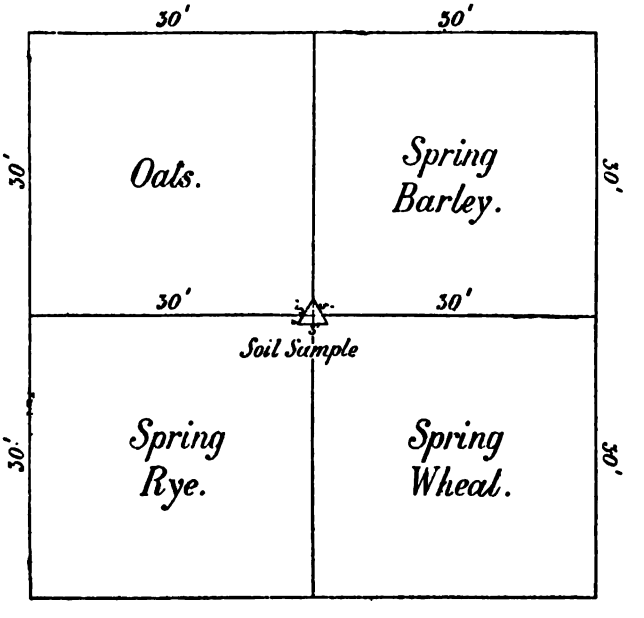
85. Sampling in Relation to Special Crop.—The special study of soils in relation to plot culture requires a special selection of samples. A method designed to meet this requirement has been devised by Moore.[66]

The chief purpose of securing the samples in the manner about to be described is to study the relation between the quantities of certain plant foods in the soil, for example, potash and phosphoric acid, and the quantities of these substances removed by the crops.

In this work it is convenient to select a part of the field appar-

[66] Circular No. 9, Bureau of Chemistry.

ently homogeneous in composition 60 feet square and divide it into four parts which may be planted with the crops indicated in the appended diagram. Each part of the plot contains nearly one-fiftieth of an acre.



In the center of the plot as indicated by the triangle the sample of soil is secured from an area formed by an equilateral triangle, each side of which is three feet in length. This triangle is so laid off as to have approximately one quarter of its area in each sub-plot. Inasmuch as the whole plot is practically homogeneous in composition the equal distribution of the area of the triangle is not of prime importance. The triangular form of area is convenient because it is easy to mark out when a properly prepared belt 9 feet long and marked at intervals of 3 feet, and pegs are sent to those charged with sampling soils and crops. One peg is driven in the ground at the appointed spot, the cord drawn taut, the second peg driven, the belt placed over the two pegs drawn taut and the third peg driven at the mark.

The soil is removed from this space to a depth of 9 inches, the pit cleaned and a subsoil sample to the additional depth of 9 inches secured. The whole of the material may be used for subsampling where a great many such samples are required. To this end each of the samples is sent to the laboratory and the part that passes a 2 mm sieve retained for subsampling.

86. **Soil Sampling** depends for its success more on the judgment and knowledge of the collector than on the method employed and the apparatus used. One skilled in the art and having correct knowledge of the purpose of the work will be able to get a fair sample with the simplest appliances while another with the most elaborate outfit might fail entirely in collecting anything of representative value.

There are some special kinds of soil sampling, however, which cannot be left to the judgment of the individual and it is believed that with the descriptions given above nearly all purposes for which samples are desired may be served.

For the study of nitrifying organisms, however, special precautions are required and these will be noted in part eighth.

For the general physical and chemical analytical work the standard methods of sampling are all essentially the same. The principles laid down by Hilgard will be found a sufficient guide in most cases.

TREATMENT OF SAMPLE IN THE LABORATORY

87. **The Sample,** or mixed sample, secured by one of the methods above described, is placed on a hard smooth surface, broken up by gentle pressure into as fine particles as possible and all pieces of stone and gravel carefully removed and weighed. All roots, particles of vegetable matter, worms, etc., are also to be weighed and thrown out. The separation can be facilitated by using a sieve of from one to two millimeters mesh. Care should be taken that all the fine soil be made to pass through, which can be accomplished by subjecting the lumps to renewed gentle pressure with a rubber-tipped pestle. In the above operation the soil

should be dry enough to prevent sticking. The relative weights of the pebbles, roots, etc., and the soil should be determined.

88. **Order of Preliminary Examination.**—Hilgard commences the examination of a soil sample by washing about ten grams of it into a beaker with a water current of definite velocity, stirring meanwhile actively the part carried into the vessel.[67] The residue not carried by the current is examined macro- and microscopically to determine the minerals which may be present, and the condition in which the fragments exist, whether sharp or rounded edges, etc.

This examination will give some general idea of the parent rocks from which the sample has been derived and of the distance the particles have been transported. Next follows the hand test, *viz.*, rubbing the soil between the thumb and fingers first in the dry state and afterwards kneading it with water and observing its plasticity. Following this should come a test of the relations of the sample to water, *viz.*, its capacity for absorbing and retaining moisture. Finally the separation of the soil into particles of definite hydraulic value and a chemical examination of the different classes of soil particles conclude the perliminary analytical work.

89. **Air-Drying.**—The sifted soil should be thoroughly mixed and about one kilogram spread thinly and left for several days exposed in a room with free circulation of air and without artificial heat. The part of the sample to be used for the determination of nitrates should be dried more quickly as described in another place. The sample is then placed in a clean, dry bottle, corked, sealed, and labeled. The label or note book should indicate the locality where the sample was secured, the kind of soil, the number of places sampled, and other information necessary to proper description and identification.

90. **The** treatment described by Caldwell requires that the stones and larger pebbles should be separated from the finer parts by hand, or by sifting with a very coarse sieve, and examined with reference to their mineralogical character, weight and size, making note, in this last respect, of the number that are as large as

[67] Journal of the American Chemical Society, 16 : 36.

the fist or larger, the number as large as an egg, a walnut, hazelnut, and pea, or give the percentage of each by weight.[68]

Pulverize the air-dried soil in a mortar with a wooden pestle, and separate the fine earth by a sieve with meshes three millimeters wide. This sieve should have a tightly fitting cover of sheepskin stretched over a hoop, and it should be covered in the same manner underneath, so that no dust can escape during the process of sifting.

Wash the pebbles and vegetable fibers remaining on the sieve with water, dry and weigh the residue; the water with which this gravel is washed should be evaporated to dryness at a temperature not exceeding 50° towards the close of the evaporation, and the residue mixed with what passed through the dry sieve.

The sifted fine earth is reserved for all the processes hereinafter described, and is kept in well-stoppered bottles, marked air-dried fine earth.

91. **Wolff** directs that the air-dried earth(in summer dried in thin layers at room temperature, in winter in ovens at from 30° to 50°) be freed from all stones, the latter washed, dried, and weighed.[69] The soil is next passed through a three millimeter mesh sieve, the residual pebbles and fiber washed, dried, and weighed. The fine earth passing the sieve is used for all subsequent examinations. It is air-dried at moderate temperatures and preserved in stoppered glass vessels.

92. **The French** Commission calls especial attention to the method of subsampling, and prescribes that the sample of earth which has been secured in the manner indicated, and of which the weight should be greater as the material is less homogeneous should not be analyzed as a whole.[70] It should be divided into two parts. The first includes the finer particles constituting the earth, properly so-called, with the elements which alone enter into play in vegetable nutrition and on which it is necessary to carry out the analysis. The second embraces the coarser particles to which only a superficial examination should be given and which may have

[68] Agricultural Chemical Analysis, 168.

[69] Zeitschrift für Analytische Chimie, 8 : 87, et seq.

[70] Annales de la science agronomiques, 8th year, 1 : 247.

a certain importance from a physical point of view but which cannot take any part from a chemical point of view, in the nutrition of plants. It is, however, useful to examine its mineralogical constitution and to look for the useful elements such as lime, potash, etc., which it may be able to furnish to the earth, and in proportion as it is decomposed, finer particles which may be useful in plant nutrition.

What is the best way to distinguish between the fine and coarse elements? All grades of fineness are observed in the soil from the particles of hydrated silica so small that with the largest magnifying power of the microscope it is scarcely possible to distinguish them, up to grains of sand which are of palpable size and visible to the naked eye, and extending to pebbles of varying sizes. All intermediate stages are found between these and if it should be asked what is the precise limit at which it is necessary to stop in distinguishing the fine from the coarse elements of the soil, the answer is that this can only be determined by a common understanding among analysts. In general, it may be said, that the mark of distinction should be the separation which can be secured with a sieve having ten meshes per centimeter.

93. **Deherain** advises that the pebbles be separated by means of a sieve of ten threads, each one millimeter in diameter, to the centimeter.[71] At the first shaking a part of the fine earth is separated but a part still remains on the sieve in the shape of small agglomerated masses. These are broken up in a mortar with light trituration, not breaking the pebbles. The pestled particles are again thrown on the sieve and the operation continued until the fine earth is separated. The residual pebbles are weighed and the weight of the fine earth determined by subtraction from the original weight of the sample. The pebbles are treated with hydrochloric acid to determine whether they are calcareous or silicious in character.

94. **Loose Soils.**—Having selected a sieve of given size, the process of separation in loose soils is as follows: The earth is exposed to the air and when the touch shows that it is sufficiently dry the conglomerated particles should be simply divided without breaking the rocky material which exists in a state of undivided

[71] Chimie Agricole, Second edition, 1902, 396.

fragments. There are some special precautions to be taken. Rubbing in a mortar must be forbidden since it reduces the earth to particles which are unnatural in size, as a result of the breaking up of the fragments consisting of the débris of rocks. When it is possible the earth should be rubbed simply in the hand and after having separated that which passes the sieve, the large particles which have not passed should be again rubbed with the hand, until all the particles which can be loosened by this simple treatment have passed the sieve. The separation should be complete in order that a sample of the particles passing the sieve should represent as nearly as possible, a correct sample of the fine particles of the soil.

In regard to the pebbles, they should be washed with water upon the sieve in order to carry through the last of the particles of earth adhering to them. They are then dried and their weight taken. The fine part of the earth is also weighed. On an aliquot part, say 100 grams, the moisture is determined and then the weight of the whole sample of the air-dry soil can be calculated to the dry state. The sample is then placed in a glass flask.

The pebbles are examined with a view of determining their mineralogical constitution; as for instance, on being touched with a little hydrochloric acid it can be determined whether or not they are carbonate of lime. The nature of the rock from which they have been derived is often to be determined by a simple inspection.

95. **Compact Soils.**—If the soils are not sufficiently loose to be treated as before described, it is necessary to have recourse to other means of division which should not, however, be sufficiently energetic to reduce the rocky elements to fine particles. For this purpose the earth may be broken by means of a wooden mallet, striking it lightly and separating the fine elements from time to time by sifting. A wooden roller may also be used with a little pressure for breaking up the particles, or a roller made out of a large glass bottle. These methods will permit of a sufficiently fine division of the soil without breaking up any of the pebbles. Sometimes, however, a soil can not be broken up by such treatment. It is then necessary to have recourse to the following process: The soil is thoroughly moistened and afterwards rubbed up with water. The paste which is thus formed, is poured upon the sieve

and washed with a stream of water until all the fine particles are removed. The wash water and the fine particles are left standing until the silt is thoroughly deposited when the supernatant water is poured off and the deposited moist earth is transferred into a large dish and dried on a sand or water-bath. In this way a firm paste is formed which can be worked up with the hand until rendered homogeneous and afterwards an aliquot portion be taken to determine moisture.

96. **Method of Peligot.**—The method recommended by Peligot for the preparatory treatment of the sample is essentially that already described.[72] The sample is at first dried in the air and then in an oven at 40°. When dry and friable 100 grams are placed in a mortar and rubbed with a wooden pestle. It is then passed through a sieve of 10 meshes per centimeter. The stones are separated by hand. They should be shaken with water in order to detach any pulverulent particles adhering thereto. The turbid water resulting from this treatment is added to that which is used in separating the sand from the impalpable part of the soil.

97. **Wahnschaffe** prescribes in the further preparation of the sample for analysis that the coarse pieces up to the size of a walnut be separated in the field where the sample is secured and their relative weight and mineralogical character determined.[73] The soil sample is then to be placed in linen or strong paper bags and carefully labelled. In order to avoid any danger of loss of label the description or number of the sample should be put on the cloth or paper directly.

The sample when brought to the laboratory should be spread out to dry, in a room free of dust. In the winter the room should be heated to the usual temperature. The air drying should continue until there is no sensible loss of weight. The samples then are to be placed in dry, glass-stoppered bottles where they are kept until ready for examination. This method of keeping the samples avoids contact with ammonia or acid fumes with which a laboratory is often contaminated.

98. **The Swedish** chemists direct that samples which are to be used for chemical examination in the manner described below, are

[72] Traité de Chimie analytique appliqué a l'Agriculture, 149.

[73] Anleitung zur wissenschaftlichen Bodenuntersuchung, 19.

most conveniently brought to such a condition of looseness and humidity that the soil feels moist when pressed between the fingers without, however, sticking to the skin.[74] To prepare the sample in this manner, spread it in a large porcelain dish or on a glass plate in a place where it is not reached by the laboratory atmosphere; stir it frequently till it assumes the mentioned humidity (if the sample when sent is too dry, moisten it with distilled water till its condition is as indicated); then pulverize carefully between the fingers and finally sift through a sieve with holes five millimeters in diameter. In this way free the sample from stones, undecayed roots and similar parts of plants, pieces of wood, and other matter strange to the soil, which remain on the sieve; mix the sample carefully and put it into a glass bottle provided with a stopper well ground in and keep it in a cool place. Samples prepared in this way will usually contain from 20 to 30 per cent. moisture, boggy soils from 60 to 80 per cent. and peaty soils 50 per cent.

99. **Petermann** follows the method outlined below in preparing samples of soil for analysis.[75]

The soil is gently broken up by a soft pestle and all débris, if of organic nature, is removed by forceps, cut fine with scissors, washed free of adhering earth dried at 120° and weighed. The nature of the organic débris should be noted as carefully as possible. About 2500 grams of this soil are passed through a one millimeter-mesh sieve.

The pebbles and mineral débris not passing the sieve are washed in a large quantity of water by decantation. They are also dried at 120° and weighed. This débris is examined mineralogically and thus some idea of the origin of the soil obtained.

100. **The** various methods for the perliminary treatment of soils as practiced by the best analysts have been somewhat fully set forth in the foregoing résumé. The common object of all these procedures is to get the soil into a proper shape for further physical and chemical examination and to determine the weights of pebbles and foreign bodies contained therein.

[74] Methods of Analysis of Soils and Fertilizers adopted by the Swedish Agricultural Chemists, translated for the author by F. W. Woll.

[75] L'Analyse du Sol, 14.

The essential conditions to be observed are the proper sifting of the material and avoidance of mechanical communition of the solid particles too large to pass the meshes of the sieve. If possible the material should be passed through a sieve of one millimeter mesh. In cases where this is impracticable a larger mesh may be used, but as small as will secure the necessary separation. Before final chemical analysis a half millimeter mesh sieve should be employed if the soil be of a nature which will permit its use. Overheating of the sample should be avoided. Rapid drying at temperatures not exceeding 50° is advisable when the samples are to be examined for nitrates.

The methods recommended seem well adapted to the general treatment of samples, but the analyst must be guided by circumstances in conducting the preparation of the sample in the laboratory or by the special object in view.

The analyst should always bear in mind, both in getting and preparing the samples the principal purposes to be served by the examination. The problems connected with the study of the soil are so complex that no hard and fixed rules can be applied in all cases. Much of the prejudice which is prevalent regarding the physical and chemical study of soils is due to the lack of care in selecting and preparing samples. It should not be forgotten that all of our exact knowledge concerning soils, their origin, character, classification and fertility, has been obtained through the media of physical and chemical study.

PART THIRD

STUDY OF PHYSICAL PROPERTIES

101. Color.—The color of a soil depends chiefly upon the proportion of organic matter and iron compounds which it contains and the state of subdivision of its particles. When a soil contains a large amount of organic matter, especially when this organic matter is in an advanced state of decay, it assumes more or less a black or brown color when moist. This black color is to be distinguished from the black alkali tint which is produced by the action of carbonate of soda on organic matter. The naturally black color of a soil containing a large amount of organic matter depends either upon the action of mineral matters upon this organic matter, as in the case of the black alkali mentioned, or upon the blackish color of carbon resulting from the slow combustion of the organic matter during the period of decay.

The presence of a large amount of ferric oxid in soil gives the well-known red color so well-marked in the soils of many portions of the United States. The preponderance of sand in a soil tends to produce a light yellow or whitish tint, while certain kinds of clay have a bluish tint probably due to the presence of ferrous salts together with some organic matter. The influence of the color of the soil upon the color of the vegetation is also well-marked, the black soils as a rule producing a much deeper green tint of foliage than the light colored soils. This effect should not be attributed to color alone for as a matter of fact highly colored soils are usually very retentive of moisture. Such soils will produce a more vigorous and ranker growth of vegetation, but it is the texture of the soil, the superabundance of plant food especially nitrogen, and the more moist condition which it maintains, rather than the color, which produce the deeper green tint of foliage.

The color of a soil is also within certain limits an index of its fertility, the black and red soils being usually the most fertile.

102. **Determination of Color.**—There is no process which will give experimentally and accurately the color of a soil sample. The changes which the color of a soil undergoes in passing from a saturated to an anhydrous state are well-marked. The analyst will have to be content with giving as nearly as possible a description of the color of the sample when received and the changes which it undergoes in air drying or on heating in a bath to 100°-110°, or in heating to redness with or without exclusion of the air. These changes in color will give some indication of the character of the organic and mineral matters present. Since the content of water influences so greatly the apparent color it is advisable to reduce all samples to the same condition of moisture for comparative purposes. There are two conditions which are easily attained, *viz.*, air-dried and saturated. Comparison of colors should be made in each of these states.

103. **Odoriferous Matters in Soil.**—It is known that the soil emits a peculiar odor which is not disagreeable and which is most intense when it has been recently wet, for instance, after a short rain. Several attempts have been made to discover the nature of this odor. These researches have established the fact that the essential principle of this odor resides in an organic compound of a neutral nature of the aromatic family and which is carried by the vapor of water after the manner of a body possessing a feeble tension. The odor is penetrating, almost piquant, and analogous to that of camphorated bodies and quite distinct from other known substances. In regard to the quantity of this substance, it is extremely minute and can be regarded as being only a few millionths of a per cent.

According to Berthelot and André[76] this new principle is neither an acid nor an alkali nor even a normal aldehyd. It is, in a concentrated aqueous solution, precipitable by potassium carbonate with the production of a resinous substance. Heated with potash it develops a sharp odor of a resinous character. It does not reduce the ammoniacal nitrate of silver. Treated with potash and iodin it gives an abundant formation of iodoform, which, however, is a property common to a great number of substances. These authorities have not found in the emanations from moist

[76] Comptes rendus, **122** : 598.

soil either furfurol, acetone or alcohol said by Müntz to exist in certain soils where moreover their existence is easily explained. They do not appear to occur generally.

For the qualitative and quantitative estimation of the odoriferous matter the following process is employed: About three kilograms of the soil, mixed with the sand containing a small amount of carbonate of lime and some humic substance characteristic of the soil of Meudon are used for the determination. After having freed it from all organic débris which is visible, it is placed in a glass alembic. The soil should contain from 10 to 12 per cent. of water at least. The alembic is placed in a sand bath and is kept at 60° for several hours. The evaporated water is condensed until about 175 cubic centimeters are distilled over. This distilled water is again rectified so as to obtain in all about 20 cubic centimeters. The odoriferous matter appears to be nearly all contained in this 20 cubic centimeters, showing its feeble vapor tension. The liquid thus obtained shows an alkaline reaction; it contains some ammonia and reduces ammoniacal silver nitrate. This last reaction is due to some pyridic alkali or analogue thereof, since when it is distilled anew with a trace of sulfuric acid it gives a neutral liquor deprived of all reducing action but which preserves the odor peculiar to the soil. The 20 cubic centimeters obtained as before are subjected to two additional distillations and in the final one only one cubic centimeter of liquid is distilled over. The peculiar odor is itensified proportionately as the volume of the liquid is decreased. To this one cubic centimeter, is added some pure crystallized potassium carbonate. The liquor is immediately troubled and some hours are required for it to become clear again. Meanwhile there is formed upon its surface a resinous ring almost invisible, amounting at most to from 10 to 20 milligrams of a matter which has not been identified with any known principle. The reactions described above, however, permit of its general character being known. This resinous matter contains the odoriferous principle, the composition of which is not yet definitely known.

104. Specific Gravity.—The density of a soil depends on its composition, the fineness of its particles and upon the packing which

it has received. It has in other words an apparent and a real specific gravity. It is easy to see that a soil in good tilth would weigh less per cubic foot than one which had been pressed closely together, as in a road or well-grazed field. Ordinary soils in good tilth have an apparent specific gravity of about 1.2, and when entirely free from air, a real specific gravity of about 2.5. If the apparent specific gravity of a soil sample were 1.2 and the air were removed, leaving a vacuum in the interstices of the soil, the apparent specific gravity would not be sensibly increased. The figure 1.2 is the apparent specific gravity of a mixture of soil material which is about 2½ times heavier than water, and of an extremely small proportion by weight of air which is about 1000 times lighter than water. The figure 2.5 is about the true specific gravity of the real soil material, except in soils containing an excessive amount of organic matter.

The weights of a cubic foot of different kinds of soil as given by Schübler[77] are as follows:

	Pounds.
Sand	110
Sand and clay	96
Common arable soil	80 to 90
Heavy clay	75
Vegetable mold	78
Peat	30 to 50

In general the specific gravity of soil decreases inversely as its content of humus.

105. Determination of Specific Gravity.—The ordinary method of proceeding to determine the true specific gravity is by means of a pyknometer. The pyknometer should have a capacity of from 25 to 50 cubic centimeters.

From 10 to 15 grams of earth dried to constant weight at 100° boiled for a time with a few cubic centimeters of water to remove air are poured into the pyknometer. All soil particles are washed out of the vessel in which the boiling takes place into the pyknometer with freshly boiled distilled water and after cooling to the temperature of the calibration of the pyknometer it is filled with distilled water at the given temperature and weighed. If the soil contain materials soluble in water in any

[77] Stockbridge: Rocks and Soils, 153.

proportion large enough to influence the results, alcohol of definitely known specific gravity may be employed and the number thus obtained calculated to a water basis.

The calculations when water is used are made as indicated in the following example:

	Grams.
Weight of pyknometer	13.4789
" " " full of distilled water at 20°	62.8934
" " water in pyknometer	49.4145
" " dry soil	10.0000
" " pyknometer + dry soil + filled with water at 20°	67.9834
" " soil and water	54.5045
" " water	44.5045
" " " displaced by ten grams soil	4.9100

Then specific gravity = 10.000 ÷ 4.9100 = 2.0367.

106. Specific Gravity of Undried Soils.—It is often desirable to determine the specific gravity on an undried portion of the soil. For this purpose a portion of the sample is dried at 100° to determine its percentage of moisture. The specific gravity is then determined on a 10 gram sample of the undried soil as just given. The actual weight of soil is calculated from the percentage of moisture obtained in the first instance. In the case given if the percentage of moisture at 100° is found to be 10 then the actual weight of dry soil is nine grams. This number is therefore used in making the calculations. In all statements of specific gravity determined in the manner described the temperature at which the pyknometer is calibrated should be stated and all weighings where water is involved made at that degree. If it is desired to refer the specific gravity made in the manner above described to any other temperature of water as for instance 4° it is easily accomplished by a simple calculation.

107. Volume of Soil.—If it be desired to calculate the volume occupied by a soil it is easily done by dividing the weight of water displaced by the weight of one cubic centimeter of water of the temperature at which the determination took place.

In the case given one cubic centimeter of water at 20° weighs 0.998259. Then 4.9100 ÷ 0.998259 = 4.9186 cubic centimeters = volume occupied by 10 grams of dry soil excluding interstitial spaces between particles. The actual volume including intersti-

tial spaces occupied by a finely divided mineral substance such as the fine earth used in soil analysis is larger when in a dry state than when saturated with water. This may be shown by grinding a rock to a fine powder and placing the dust in a graduated cylinder, and shaking the cylinder to constant volume. The same volume of the dust when thoroughly saturated with water will be found to occupy a smaller volume. The fine soil therefore tends to become more compact when wet than when partially dry.

108. Volumetric Methods.—The water displaced by a given weight of soil may also be measured volumetrically by the method of Knop[78] slightly modified to secure greater simplicity.

Place 200 grams of the dry soil in a flask of 500 cubic centimeters capacity. Add a measured quantity of water, and shake thoroughly to eliminate air, and fill up to the mark from a burette. The quantity of water required to complete the volume subtracted from the number expressing the volume of the flask will give the volume of water displaced by the earth.

Another method consists in thoroughly shaking about thirty grams of the soil in a graduated cylinder with 50 cubic centimeters of water containing a little ammonium chlorid and after 24 hours recording the volume occupied by the whole. The increase in volume over 50 cubic centimeters shows the quantity of water displaced. This method may also be used to determine the volume occupied by a soil when saturated with water. The above methods are only to be used when approximately correct results are all that are desired.

109. Apparent Specific Gravity.—The apparent specific gravity of a soil is obtained by dividing its volume, interstitial spaces included, by the weight of an equal volume of water.

The real and apparent specific gravities of six samples of soil are given below:[79]

	1.	2.	3.	4.	5.	6.
Real specific gravity	2.5445,	2.6315,	2.6508,	2.6400,	2.7325,	2.6603
Apparent specific gravity of air dried soil	1.0940,	1.1710,	1.3570,	1.2810,	1.4060,	1.2735
Apparent specific gravity of soil dried at 125°	1.0990,	1.1770,	1.3750,	1.2910,	1 4640,	1.2800

[78] Die Landwirtschaftlichen Versuchs-Stationen, 8 : 40.

[79] König, Landwirtschaftlich und Gewerblich Wichtige Stoffe, 2d Edition, 47.

It is to be noted that in computing the apparent specific gravity of a soil dried at 125° the volume occupied by the water is assumed to occupy the same space as if it existed in a free state. The volume of this water is therefore to be subtracted from the contents of the flask before proceeding with the computations.

110. Determination of Weight per Hectare or Acre.—Place in small quantity at a time portions of the air-dried sample properly prepared in an open cylinder, holding one liter, and about 170 millimeters high (if the height is exactly the mentioned one, the diameter of the cylinder will be 86.6 millimeters); pack the sample by striking the bottom of the cylinder hard against the palm of the hand after each new filling and weigh on a balance sensitive to 0.1 gram. The weight of one liter of soil in approximately similar conditions as it is found on the dry land prepared for cultivation, is thus ascertained. The weight of one liter of the soil in grams multiplied by 2000 will give in kilograms the weight of the surface soil from a hectare (2.47 acres) of the field from which the sample is taken to the depth of 20 centimeters.[80]

RELATION OF THE SOIL TO HEAT

111. Sources of Soil Heat.—The heat of the soil comes from three sources, *viz.:* solar heat, heat of chemical action within the soil, and the original heat of the earth's interior. The latter is sensibly a constant quantity, and of great value to plants. The heat of chemical action is not great in amount except in a few special cases but is often, as in germination, of the greatest importance to plant growth. The sun, therefore, remains the greatest source of heat of practical importance in relation to the production of crops. Dark-colored soils, absorbing most and radiating the fewest rays, must attain the highest temperature. Schübler's classical researches on soil temperatures, show that there is at times a difference of over 7° in temperature between white and black soils, all other conditions being alike. Schübler's reseaches, made on dry soils in the laboratory, are not to be applied too rigidly to conditions in the field.

[80] Methods of the Swedish Agricultural Chemists, translated for the author by F. W. Woll.

112. **Influence of Specific Heat.**—The quantity of heat which a soil receives and retains is determined in given conditions by its specific capacity for heat. The specific heat of a body is expressed by a number which shows the amount of heat necessary to raise a given weight of the body 1° of temperature, as compared with the amount necessary to raise the same weight of water 1°. The specific heat of the soil is usually between 0.20 and 0.25 when that of water taken as the standard is unity.

113. **Influence of Moisture.**—The moisture of the soil possesses great influence on the soil temperature, so much so that a dry, light-colored soil may attain a greater degree of warmth than a moist, dark-colored one. The wetter the soil the larger the quantity of heat required to raise the temperature to any given degree. The action of water in reducing soil temperature is easily explained. In our latitude, we see the water in all its forms, solid, liquid, and gaseous, and we know that these forms are the direct result of temperature. The changing of water from the solid to the liquid or gaseous form is performed at the expense of heat; the more water evaporated from the soil the more heat must be used for the evaporation. Therefore, the more water contained in the soil at any given time the lower must be its temperature during subsequent exposure to sun heat because of the greater evaporation. The experiments of many careful investigators have practically settled all the important questions of soil temperature. The radiation of heat from the soil, and the consequent cooling propensity of the latter, are directly proportional to the absorptive power of the soil. Two soils of like absorptive power towards heat possess, as a rule, equal radiating power.

In a general way, it can be said the greater the heating capacity and conductivity of a soil the more readily and rapidly does it give off its heat and become cooled.

114. **Absorption of Solar Heat.**—The quantity of heat absorbed from the sun by the earth is an important factor in the growth of vegetation. As has been established in the physics of heat, a black surface, other things being equal, will absorb a larger amount of heat than one of any other color; so, other things being equal in the physical and chemical composition of a soil, variations in the amount of organic matter producing greater or less black color-

ation will affect the heat absorption. Thus, black soils, in the conditions above mentioned, will absorb more heat than lighter colored soils. As a result, the vegetation in such soils gets an earlier start in the Spring and matures more rapidly. As an illustration of this it may be noted that the black prairie soils of Iowa produce uniformly crops of maize which are matured before the early frosts, while crops grown on lighter soils much farther south often suffer injury from that source.

DETERMINATION OF SPECIFIC HEAT

115. General Principles.—The quantity of heat stored in any given weight of soil is capable of being measured and compared with the quantity stored in an equal weight of water at the same temperature. The ease, however, with which disturbing influences operate during the determination makes the manipulation somewhat difficult. The specific heat of the containing vessels must be carefully determined. Fortunately this has been done for most materials and the data thus obtained are recorded in standard works on physics. The material operated on must be protected from thermal influences from sources not controlled by the experiment and even the heat of the operator's body may often disturb the conduct of the work. The general conditions which should control the experiment as well as the details thereof are given in the following method which, however, the ingenious analyst may profitably simplify.

116. Method of Pfaundler.—The process of estimating the specific heat of soils by the method of mixture, is essentially that of Regnault and is described as follows by Pfaundler.[81]

The apparatus used is illustrated in Fig. 11.

A and A_1 show the heating apparatus. It consists of a vessel of sheet iron in which a test tube E is fixed by means of a cork. The test tube holds the soil whose specific heat is to be determined. The apparatus contains water, which is brought to the boiling point by means of a lamp, and the excess of steam is conducted away, as indicated in the figure, through one of the axes of the apparatus; the opposite axis is, of course, closed. It requires

[81] Poggendorf's Annalen der Physik und Chemie, 1866, [5] 9 : (128), 102, et seq.

about 35 minutes boiling to bring the contents of the test tube to the temperature of the aqueous vapor. To avoid the effect of radiation the apparatus above the water line should be covered with cotton or some other non-conductor of heat. The exact temperature at which the water boils is determined by observing the barometer at the time and consulting a table of the boiling temperature of water at different barometric pressures.

The calorimeter is shown in the figures B and B_1. It consists of a wooden box closed on one side by a glass plate G and on the other to the height F by a small board on which a calorimeter of ordinary construction is placed. The inner thin-walled cylinder of the calorimeter is 70 millimeters high and 47 millimeters in diameter. The outer envelope of the calorimeter is correspondingly wider and deeper.

Both parts of the apparatus are supported by triangular pieces of cork. A delicate thermometer is fastened to the top of the box of the calorimeter and the value of the degrees is so arranged that about twelve of them correspond to about one degree C. The scale of the instrument can be arbitrarily fixed and the temperature of any part of it determined by comparison with a delicately graduated thermometer.

Near the thermometer in the calorimeter is a perforated stirrer made of a very thin copper disk with a bent rim. This stirrer is operated by means of a silk cord moved by appropriate machinery. The advantages of the apparatus over Regnault's consists in having the calorimeter stationary and in the facility with which the heated sample can be introduced into the calorimeter so as not to sensibly influence the results by any heat that might come therefrom.

The reading of the thermometer is made through a glass plate and this should be protected from the heat of the body of the observer by a paper screen.

The test tube E is first filled with the substance, whose specific heat is to be determined, and weighed. It is then placed in the water bath until constant weight is reached. After constant weight has been obtained the apparatus is again weighed and the exact weight of the moisture lost thus determined. The test tube is then placed in the apparatus A closed with a well-fitted cork,

the top covered with cotton and heated in the aqueous vapor for

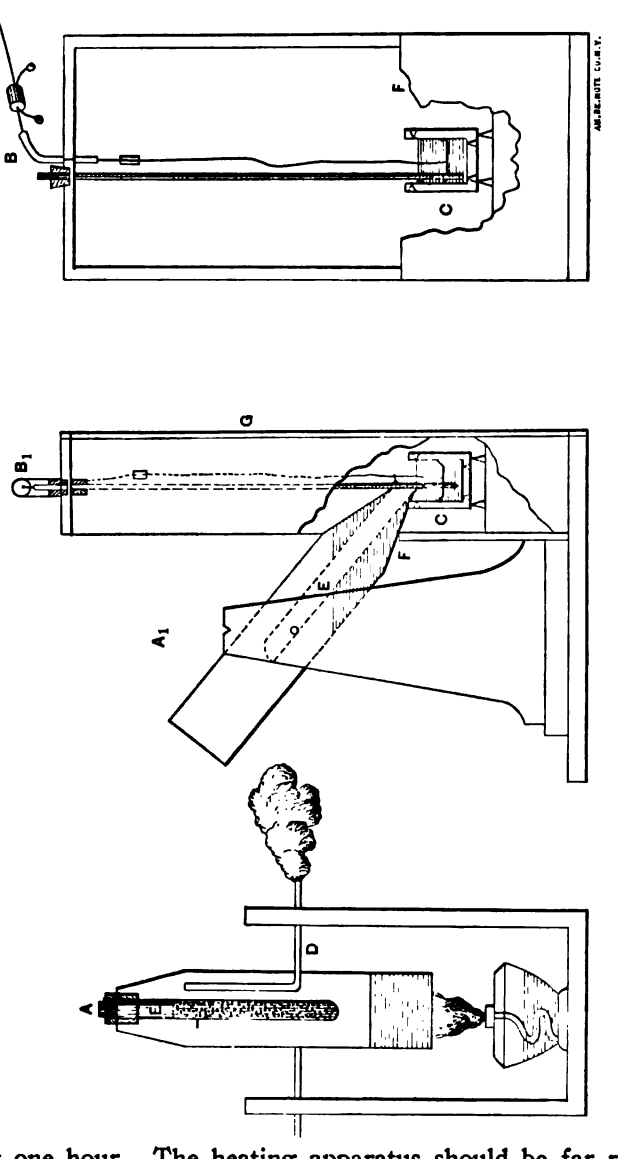


FIG. 11.
REGNAULT'S APPARATUS FOR DETERMINING THE SPECIFIC HEAT OF SOILS.

about one hour. The heating apparatus should be far removed

from the calorimeter and screened so that the temperature of the latter cannot be influenced thereby. Meanwhile the calorimeter is filled with water which has stood in the room for a long time until it has acquired, as nearly as possible, the room temperature.

The quantity of water is such that the water value of the whole of the calorimeter together with the immersed portions of the thermometer and stirrer shall amount to exactly 100 grams of pure water. A few minutes before bringing the substance into the calorimeter, the stirring apparatus is put in motion and the temperature observations are commenced. These should be at intervals of 20 seconds and should be continued until 10 observations have been made. Meanwhile the height of the barometer is also read. A few seconds before the tenth interval the apparatus A is brought quickly to the calorimeter and its contents emptied into it at the moment of the tenth interval. The apparatus A should be removed as quickly as possible after its contents are emptied.

After the introduction of the substance and its thorough incorporation with the water of the calorimeter by the stirring apparatus, the thermometer is again read, at intervals of 20 seconds, until its maximum has been reached and as much longer thereafter as may be necessary to show that an appreciable fall of temperature has taken place. The test tube, in which the substance was heated is weighed and the exact quantity of the added substance thus determined. In inverting the test tube to deliver the heated soil to the calorimeter care is taken that no part of the apparatus A touches any part of the calorimeter. To aid in this a cork shield should be fixed on the board F at a convenient height.

In order that the sample of soil may be easily removed from the test tube in which it is heated, it is best to have it molded into appropriate forms before being placed in the heating tube. This is easily accomplished by pressing it into molds of convenient shape and of a size so that six or eight pieces (best of cylindrical shape) will be necessary to give the quantity sufficient for the experiment. Since some soils will not retain their shape after molding, the molds may be made of zinc foil whose water values in the calorimeter are previously determined and they can be placed with their contents in the calorimeter thus securing the

total immersion of all the particles of soil in the water. This is important with certain soils rich in humus and with peats which in a dry state will not sink unless thus weighted. With very dusty materials, it is necessary that these little cylinders should be closed with pieces of foil at the ends in order to prevent the particles of dust from escaping and rising to the surface of the water. The greatest care should be taken to avoid splashing the water in the addition of the tablets of soils. It is sometimes advisable to remove the test tube from the rest of apparatus A and manipulate it by hand.

Another source of error consists in the solution of the soluble salts which the soil may contain. This is avoided by the use of turpentine instead of water. If the cylinder containing the soil be made water-tight, this danger from the solubility of the salts in water is avoided. Another method of correcting these errors is in making a blank experiment in which a quantity of the earth taken is kept at the temperature of the water in the calorimeter until both are of the same temperature. The earth is then mixed with the water and the change of temperature produced noted. In this way the corrections made necessary by the solution of the salts in water and other causes are determined.

117. **Method of Calculating Results.**—Let t represent the mean temperature of the beginning period of the experiment, and v equal the loss in heat per interval. Let t′ and v′ represent the same values for the end period. Let θ_1, θ_2, θ_3, etc., represent the temperature at the end of the first, second and third intervals of the middle period and θ_0 the temperature at the beginning of the middle period and θ_n the end temperature of the middle period. Let τ_1, τ_2, τ_3, $\cdots\cdots$ τ_n represent the mean temperatures of the single intervals; then $\tau_1 = \frac{\theta_0 + \theta_1}{2}$; $\tau_2 = \frac{\theta_1 + \theta_2}{2}$, and $\tau_n = \frac{\theta_{n-1} + \theta_n}{2}$. C represents the correction which must be applied in order to determine the true increase of temperature in the calorimetric system. The expression $\theta_n - \theta_0 + C$ represents the true temperature increase of the calorimetric system which we may represent by $\Delta\theta$, and $\theta_n + C$

represents the true maximum, that is, the end temperature, which by exclusion of external influences is reached. The correction C, as already indicated, is to be added to $\theta_n - \theta_0$ when it is positive and is to be subtracted therefrom when it is negative. The numerical value of C is usually very small, and, in the experiments indicated, varies between zero and one division of the thermometer employed, and seldom reaches two divisions. Let v = the mean loss of temperature per interval in the first period and v' the same for the end period.

Then the value of C may be computed according to the following formula:

$$C = nv + \frac{v' - v}{t' - 2}\left[\theta_1 + \theta_2 + \theta_3 + \ldots + \theta_{n-1} + \frac{\theta_1 + \theta_n}{2} - nt\right]$$

from which

$$C = nv + \frac{v' - v}{t' - t}\left(\sum'_{n-1} \theta + \frac{\theta_0 + \theta_n}{2} - nt\right)$$

118. **Illustration.**—This method of determining the value of specific heat is best illustrated by an example:

In one determination the water value of the calorimetric system, including stirrer and thermometer was 2.50 grams, the weight of water added was 97.50 grams and the total water value of the system 100 grams. The substance was dried at 100° and weighed in five envelopes:

Total weight	31.423 grams
The envelopes alone weighed	10.654 "
Weight of soil	20.769 "

The envelopes holding the soil were made of brass, the specific heat of which is 0.0939 and the water value of the whole of the envelopes was 1.0004 grams. Since, however, the ends were soldered on with tin the true water value was somewhat smaller being equal to 0.8692 gram. The data of the observations were as follows:

Corrected height of barometer	699.6 millimeters.
Intervals between the observations	20 seconds.

	No. of Observations.	Temperature on the arbitrary scale of the thermometer.	
First Period	0	162°.6	
	10	162°.9 $=\theta_0$	(Moment of immersion).
Second Period	11	185°.0	
	12	200°.0	
	13	206°.1	
	14	209°.5	
	15	210°.7	
	16	211°.3	Differences.
	17	211°.5	0
	18	211°.5	0
	19	211°.5	0
	20	211°.5	0
	21	211°.5	−0°.1
	22	211°.4	$=\theta_n$
Third Period	23	211°.3	−0°.1
	24	211°.2	−0°.1
	25	211°.1	−0°.1
	26	211°.0	−0°.1
	27	210°.9	−0°.1
	28	210°.8	−0°.1
	29	210°.6	−0°.2
	30	210°.5	−0°.1

From the twenty-second interval, the regular fall of temperature begins and 211°.4 is therefore taken as θ_n. The mean temperature of the beginning period is therefore $\frac{162°.6 + 162°.9}{2}$ $= 162°.75 = t$. The value of v is $\frac{162°.6 - 162°.9}{10} = -0°.03$. For the end period the value of t' is $\frac{211°.4 + 210°.5}{2} = 210°.95$ and the value of v' is $\frac{211.4 - 210.5}{8} = +0.11$. Then the sum of the observations from 11 to 21 inclusive $= \Sigma'_{n-1}\theta \ldots 2280.1$.

$\frac{\theta_0 + \theta_n}{2} =$	187.15
The sum = ...	2467.25
$n = 12$	
$nt =$	1953.00
Difference	514.25
This difference multiplied by $v - v' =$	0.14
gives a product equal to	71.995
This product divided by $t' - t =$	48.20
gives a quotient equal to	1.49
$nv =$	−0.36
The sum = ...	1.13 = C

Then $\Delta\theta = \theta_n - \theta_0 + C = 211°.4 - 162°.9 + 1°.13 = 49°.63$. The true end temperature $= \theta_n + C = 212°.53$. The zero point of the thermometer $= 24°.70$, and the actual rise of temperature $= 187°.83$. The rise of temperature due to the proximity of the warming apparatus at the beginning was found by experiment to be equal to 0°.1 of the division of the scale. On comparing the thermometer used with a standard centigrade scale it was found that one division of the calorimetric thermometer was equal to 0°.0858. Converting these numbers into expressions of the centigrade scale we have the following summary:

The true rise of temperature, $\Delta\theta =$	4°.25
The true end temperature, $\theta_n + C =$	16°.10
The temperature of the steam, as determined by the height of the barometer, was equal to	97°.70

From these data the specific heat is calculated according to the following formula:

$$S = \frac{1}{20.769}\left(\frac{100 \times 4.25}{97.70 - 16.10} - 0.8692\right) = 0.2089.$$

From this formula the following rule for calculating specific heat is deduced:

Multiply the water value of the calorimetric system by the true rise in temperature in degrees Celsius and divide the product by the difference between the temperature of boiling water under the conditions of the experiment and the true end temperature. From the quotient subtract the water value of the envelopes holding the soil sample. Divide the remainder by the weight of soil in a dry state.

119. **Method of Lang.**—Lang has made use of a somewhat simpler form of apparatus in securing the specific heat of soil samples.[82]

The apparatus employed consists of a heater, made of heavy sheet iron Fig. 12 forming an air bath with double walls. The bottom forms a movable door, in which open two tubes for carrying a thermometer *c* and a gas regulator *d*. On *S* is fixed *an arm* carrying a hook *f* to which is attached a fine wire to support the

[82] Forschungen auf dem Gebiete der Agricultur-Physik, 1, 109.

body to be heated and passing freely into the heating chamber at *a*. A movable wire gauze *e e* aids in regulating the temperature.

The calorimeter shown in vertical section is formed of two vessels *m* and *n* made of thin polished brass. Conduction between the inner and outer parts is prevented by wood or cork plugs at *o* and *p p*, and the calorimeter is fixed to a sliding base which permits it to be brought under the air bath at the proper moment.

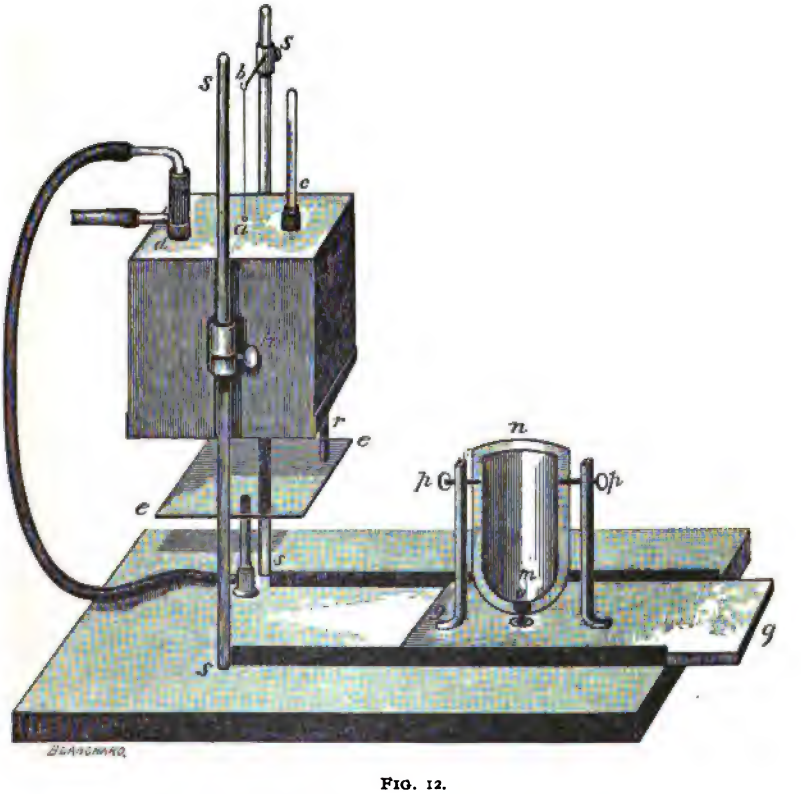


FIG. 12.

To bring the heated sample into the calorimeter the wire gauze *e e* is removed and with one hand the operator shoves the calorimeter under the air bath by which motion the movable bottom is opened by the peg *r;* with the other hand the wire holding the sample is cut allowing the sample to fall into the calorimeter. The

whole operation should not consume more than 5 seconds. The temperature of the water in the calorimeter and the water value of the whole apparatus is obtained in the manner already described. The calorimeter is covered by a perforated glass plate, not shown in the figure, previous to and after the introduction of the sample.

The samples are conveniently held in light glass-stoppered (water-tight) bottles. The heat value of the bottle and attached wire are determined and allowance made therefor in the calculations.

The specific heat is calculated according to the following formula:

$$S = \frac{(P + p_c + p_t)\ (\tau - t) - p_g .\ s'\ (T - \tau)}{p\ (T - \tau)}$$

In this formula P = weight of water in calorimeter
p = net weight of sample
p_c = water value of the calorimeter
p_t = water value of the thermometer
p_g = weight of the glass container
s' = water value of container
T = constant temperature of the air bath
t = beginning temperature of calorimeter
τ = end temperature of calorimeter

120. **Variations in Specific Heat.**—Different soils deport themselves very differently in respect of specific heat. In a large number of soils examined by Pfaundler, the specific heats were found to vary from 0.2081 to 0.5069. The highest specific heat was observed in the case of a peaty soil. Next to peaty soils came those soils which were highest in humus, and in general it was found that the specific heat varied directly with the humus content. The lowest specific heats are found in soils composed chiefly of sand.

SOIL THERMOMETRY

121. **General Principles.**—The measurement of the temperature of the soil at stated depths is often of use in analytical processes connectetd with agricultural chemistry and physics. The general principles on which the process rests, depend on bringing the bulb of the thermometer into as intimate contact as possible with the

particles of soil at the depth required, disturbing as little as possible the normal state of the soil particles.

In the thermometer chiefly used for this purpose in this country, the stem is strong and carries the degrees figured on the glass. The whole is enclosed in a wooden case which is cut away to expose the face of the scale. The scale is about eleven inches long. The part which enters the soil is of varying lengths, according to the depth at which the temperature is desired.

122. **Method of Procedure.**—An excellent method of determining soil temperatures and of recording results is well illustrated by Frear.[88]

The thermometers are set in niches cut in a trench, the earth being afterwards carefully tamped about the bulbs to secure a good contact, the trench being filled at the same time. The surface of the soil is freed from vegetation and kept in good tilth.

The depths at which observations are made are at the surface and one, three, six, 12 and 24 inches. The soil for which the following illustrative data are given was moderately dark and loamy to a depth of seven inches and below that a stiff clay. Solid rock existed at from five to seven feet below the surface. Readings were made three times a day.

123. **Method of Stating Results.**—The individual readings of the thermometers should be entered at the time they are made. At the end of each month the mean of the readings should be determined, together with the maxima and minima, and a comparison made between the mean readings of the temperature of the air and maxima and minima. The determination of soil temperatures is particularly useful in their relations to germination and the early growth of plants. Often it will prove useful to determine the proper time for planting. As an illustration of the method of stating these mean results the data are given for the month of May for the atmsophere, surface, and for the depths of soil mentioned above:

[88] Report of the Pennsylvania State College, 1891, 194.

MAY.

Atmosphere.	*T° Fahrenheit.* Degrees.
Monthly mean	57.1
Maximum	85.0
Minimum	31.0
Mean daily range	22.5
Greatest daily range	32.0
Least daily range	8.0
Surface.	
Monthly mean	56.7
Maximum (10th of month)	77.0
Minimum (5th)	36.0
Mean maximum	65.2
Mean minimum	49.9
Monthly range	41.0
Mean daily range	14.9
Greatest daily range (19th)	25.0
Least daily range (21st)	4.0
At Depth of One Inch.	
Monthly mean	56.8
Maximum (10th)	74.5
Minimum (5th)	36.5
Mean maximum	62.9
Mean minimum	49.5
Monthly range	38.0
Mean daily range	11.9
Greatest daily range (10th and 19th	20.0
Least daily range (23rd)	1.0
At Depth of Three Inches.	
Monthly mean	56.7
Maximum (31st)	71.0
Minimum (6th)	40.0
Mean maximum	60.9
Mean minimum	49.7
Monthly range	31.0

	T° Fahrenheit.
Mean daily range	9.3
Greatest daily range (19th)	15.5
Least daily range (23rd)	1.5
At Depth of Six Inches.	
Monthly mean	56.3
Maximum (31st)	66.0
Minimum (6th and 7th)	43.0
Mean maximum	56.7
Mean minimum	53.2
Monthly range	23.0
Mean daily range	4.65
Greatest daily range (8th and 19th	8.5
Least daily range (5th)	1.0
At Depth of Twelve Inches.	
Monthly mean	55.6
Maximum (31st)	64.0
Minimum (6th and 7th)	46.0
Mean maximum	56.6
Mean minimum	54.4
Monthly range	18.0
Mean daily range	2.18
Greatest daily range (8th).	4.5
Least daily range (3rd and 20th)	0.0
At Depth of Twenty-four Inches.	
Monthly mean	53.1
Maximum (31st)	58.0
Minimum (6th and 8th)	48.0
Mean maximum	53.4
Mean minimum	52.8
Monthly range	10.0
Mean daily range	0.48
Greatest daily range (23rd)	2.0
Least daily range (on 12 days)	0.0

124. **Method of Whitney and Marvin.**[84]—The soil thermometer modified by Whitney and Marvin is shown in Fig. 13. The principle on which this modification depends is as follows:

[84] Agricultural Science, 8 : 28.

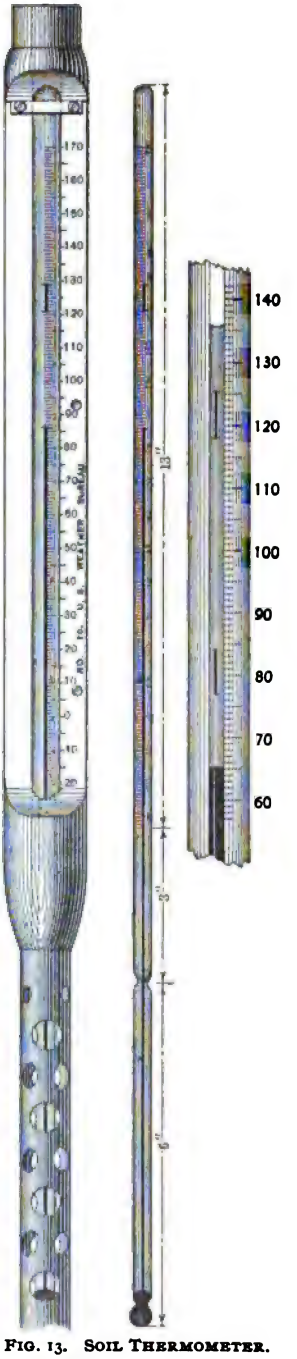


FIG. 13. SOIL THERMOMETER.

A mercurial thermometer of the ordinary construction is liable to give wrong indications of the temperature because it is difficult to determine the temperature of the column of mercury from the bulb to the surface of the ground. To avoid this source of error the thermometer figured was constructed.

The bulb of the thermometer is made quite small and a slender portion of the stem extends into its spherical portion in order to pass though the alcohol in the upper part of the bulb and extend into the mercury. The top portion of the thermometer stem does not differ in any essential respect from the stem of an ordinary thermometer.

The bulb is almost wholly filled with alcohol, which acts as the principal thermometric fluid and has the advantages of a high coefficient of expansion. The rest of the bulb and the stem of the thermometer up to a point convenient for graduation, are filled with mercury. The peculiar construction at this point is for the purpose of retaining the mercury about the point of the slender capillary stem inside the bulb and preventing the entrance of alcohol into that part of the stem when the thermometer is placed in a horizontal position.

In order to register the maximum and minimum temperatures a short column of alcohol is placed in the upper portion of the stem, above the mercury, and within this are arranged two small steel indexes, so constructed that they will not slide in the tube of their own weight, but are easily pushed upward by the mercury column or pulled downward by the top meniscus of the alcohol column. The indexes are set by means of a small magnet, the one being drawn down upon the top of the mercurial column and the other raised up against the meniscus of the alcohol column.

The rise of the mercury carries its index upward, leaving it to register the highest point reached, while the alcohol meniscus withdraws the other index and leaves it at a point representing the minimum temperature. It remains only to mention that the graduations are fixed in the usual way, having reference only to the positions of the mercurial column. Beyond the highest point supposed to be reached by the mercury, say about 120°, the graduations are extended in an arbitrary manner. The scale numbers represent temperatures by the mercurial column and are

continued in regular sequence beyond the 120°. On this plan the readings for minimum temperatures are on a purely arbitrary scale and are converted into true degrees of temperature by use of a table prepared for each thermometer, which table embodies as well all the corrections for instrumental error.

The arrangement of the alcohol column above the mercurial column and the indexes are shown enlarged at one side of the illustration. The readings of the maximum temperature are made from the bottom end of the index next to the mercurial column. The minimum temperature is the reading of the top of the uppermost index. Thus in the figure the maximum temperature indicated is 76.5°, and the minimum 125.7°, which, by reference to the table of correction for this thermometer, No. 10, is found to be 53.3°.

The use of mercury in the stem of the thermometer not only admits of the use of the index for registering the maximum temperature, but possesses the additional advantage of reducing the error due to uncertain temperature of the stem to about one-sixth what it would be if alcohol were used. Moreover, if necessary, as in the case with thermometers for greater depths than that figured, the ungraduated portion of the stem can be made of very much finer bore than the graduated portion, the effect of which is to diminish the objectionable error to a compartively unimportant quantity.

The chief objection to thermometers of this construction is the liability of alcohol getting into the stem during the processes of construction, graduation and subsequent handling, and the difficulty of safely shipping them.

When once set up, however, there seems to be little or no possibility of derangement and the error common to mercurial thermometers due to rise of the freezing point with age does not apply owing to the high coefficient of expansion of the alcohol used in the bulb.

125. General Statement.—The form of thermometer employed is not of so much importance as the accuracy with which it is graduated and its intelligent use. Soil temperatures are of great importance in plant growth from the time of germination

of the seed until maturity is reached. They have most intimate relations also to bacterial growth upon which the fertility of the soil so greatly depends. The study of soil temperatures therefore is required in a systematic knowledge of the conditions of plant growth as influenced by the varying degrees of heat in the soil.

126. Applications of Soil Thermometry.—The estimation of the rapidity of absorption of heat by soils is conveniently made by means of a cubical zinc box, six centimeters square, which is filled with the sifted air-dried soil. The box, one side of which is left open, is encased snugly in a wooden cover, exposing only the open end, and placed for a few hours in the direct rays of the sun. The temperature is then observed at a given depth. The box may be provided with thermometers at different depths, the bulbs thereof extending to the center. In this case the box should be covered with thick felt instead of wood. The temperature of the layers of soils of different depths can thus be read off directly. The air temperature directly above the box should be accurately noted while the experiment continues.

Any other kind of box well protected against all heat save the direct sunlight on the open surface of the soil will answer as well as the one described.

To determine the action of moist earth in similar conditions the soil may be used in a wet state; the per cent. of moisture being determined in a separate portion of the soil or the amount of water added to the air-dried soil being noted.

127. Estimation of the Rapidity of Conductivity of Soils for Heat.—The bulb of a thermometer is placed in the middle of a mass of fine earth which is then exposed, best in a metallic box painted with lamp black, in a warm place. The time required for the thermometer to reach a certain degree is noted. By reversing the experiment and placing the mass of earth heated to a given degree in a cool place the speed of radiation can be determined by the time required for the mercury in the thermometer to fall to any given point.

The experiment may also be made by packing the soil by gently jolting it in a glass tube from six to eight centimeters in diameter. One end of the tube is closed with a piece of metal or fine

wire gauze painted with lamp black and is exposed to the source of heat. The bulb of a thermometer is placed at a given distance from the end of the tube and the time required for the mercury to be affected observed.

COHESION AND ADHESION OF SOILS

128. Behavior of Soil After Wetting.—The deportment of a soil when thoroughly wet in respect of its physical state on drying out is a matter of great practical concern to the agronomist. Some soils on becoming dry fall into a pulverulent state and are easily brought into proper tilth; others become hard and tenacious, breaking into clods and resisting ordinary methods of pulverization. The physical laws which determine these conditions depend largely on the principles of flocculation soon to be described. The present task is to describe briefly some of the methods of estimating the force of cohesion and adhesion.

129. General Method.—The fine air-dried earth is mixed with enough water to make a paste and molded into forms suitable for trial in a machine for testing strength of cement, etc. The forms most used are cakes from three to five centimeters in length and from one to two centimeters thick. These are used for determining crushing power. For the determination of longitudinal adhesion the paste may be molded in prismatic or cylindrical shape.[85] The prisms should show from one to two centimeters in cross section or the cylinder be from one to two centimeters in diameter. Before use they are to be exposed for several days until thoroughly air-dried. The force required to separate or crush these prepared pieces will measure the adhesive or cohesive property of the sample. A great number of trials should be made and the mean calculated.

130. Methods of Conducting Tests in Bureau of Chemistry.—The general and particular methods of conducting tests of cohesion and adhesion of molded fine rock material and earth have been worked out in detail in the road material laboratory (division of tests) of the Bureau of Chemistry.[86]

[85] Haberlandt, Forschungen auf dem Gebiete der Agricultur-Physik, 1 : 148.

[86] Bulletin No. 79, Bureau of Chemistry, 25.

The cementing value of a prepared cylinder of fine earth is a useful measure of its adhesive qualities. This is determined in this Bureau as follows:

CEMENTATION TEST.[a]

The binding or cementing power of rock dust is such an important element in road building that much time has been spent in the endeavor to devise a suitable test for determining the degree to

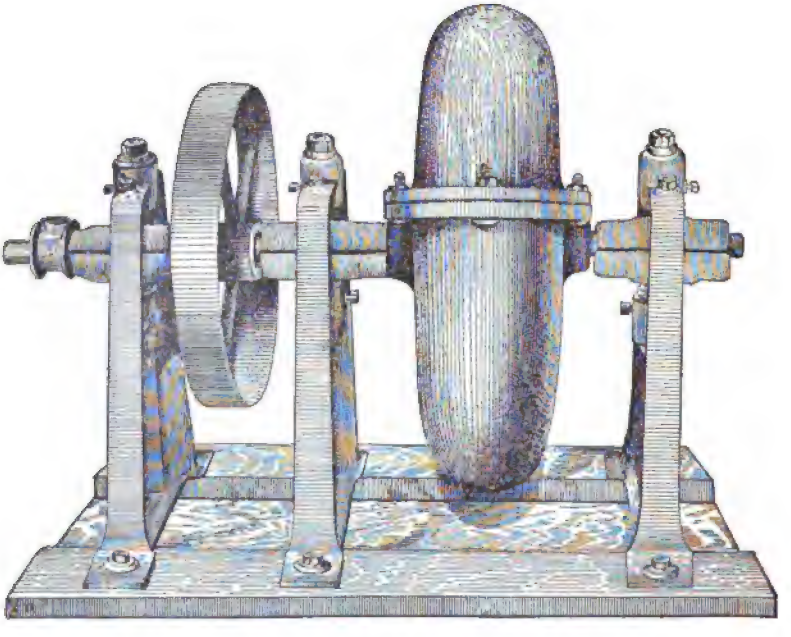


Fig. 14.

which the various rocks and gravels possess this property. Many tests have been tried, but as yet only an impact test, carried on in a uniform manner as described below, has given satisfactory results.

a This test, and the necessary machines for conducting it, were designed and developed by Page for the Massachusetts Highway Commission and the Road Material Laboratory. The impact machine at present used was built especially for this laboratory by the Maryland Geological Survey, under the direction of Mr. A. N. Johnson, highway engineer to the survey, who made several useful modifications in the machines.

One kilogram of the rock to be tested is broken sufficiently small to pass a 6 mm., but not a 1 mm. mesh screen. It is then placed in a ball mill and is ground for two hours and a half. This ball mill, shown in Fig. 14, contains two chilled iron balls which weigh 25 pounds each, and is revolved at the rate of 2,000 revolutions per hour. It was found by experiment that grinding rock thus prepared for two hours and a half was sufficient to reduce it to a powder that would pass through a 0.25 mm. mesh. The rock dust or fine earth is mixed with water to the consistency of a stiff dough and is kept in a closed jar for twenty-four hours. About 25 grams of this dough are placed in a cylindrical metal die, 25 mm. in diameter, which can be seen in Fig. 15. A closely fitting

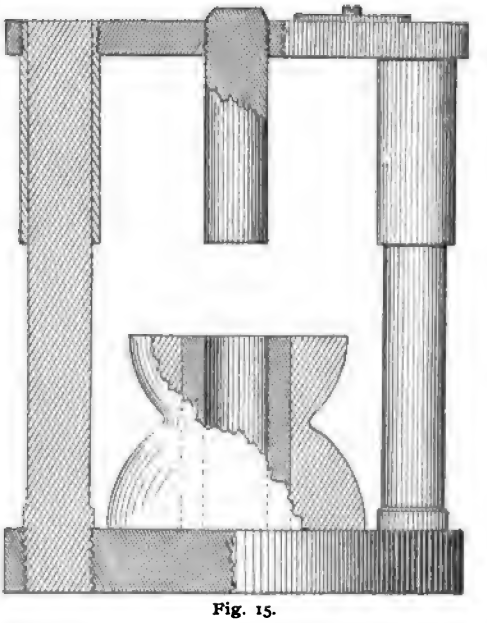


Fig. 15.

plug, supported by guide rods, is inserted over the material, which is then subjected to a pressure of 100 kg. per square centimeter.

It is most important that these briquettes should be compressed in a uniform manner, and for this a special machine has been designed (Fig. 16). The die is placed on an iron platform supported by a piston rod, which is connected directly with a hydraulic pis-

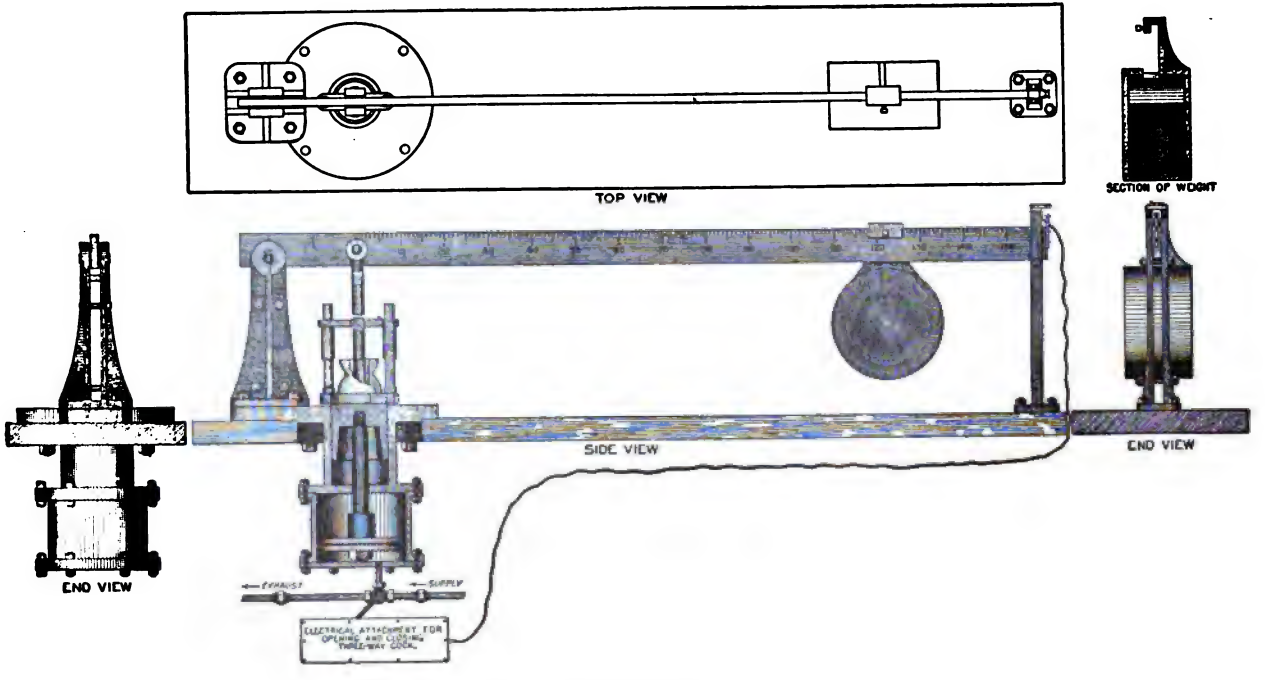


Fig. 16. Briquette Machine.

ton below. Water from a tank is admitted to the hydraulic cylinder through a small orifice in the pipe. As the piston rises the platform and die are carried up with it, the plug of the latter coming in contact with a yoke attached to a properly weighted lever arm. When the lever arm is raised one-eighth of an inch it closes an electric circuit which trips a right-angle cock, shutting off the water and opening the exhaust. One minute is required to compress a briquette, and the maximum load is applied only for an instant. By this device practically uniform conditions are obtained.

The height of the briquette is measured, and if it is not exactly 25 mm. the requisite amount of material is added or subtracted to make the next briquette the required height. Five briquettes are made from each test sample, and allowed to dry twelve hours in air and twelve hours in a steam bath. After cooling in a desiccator they are tested by impact in a machine especially designed for the purpose (Fig. 17). It consists of a 1 kg. (2.2 pounds) hammer *(H)*, which is guided by two vertical rods *(D)*. The hammer *(H)*, which ends in a small cone at the top *(L)*, is caught on the lower side of the cone by two spring bolts, and is lifted by a crosshead *(I)* which is joined to a crank shaft above. A vertical rod *(P)*, which is directly over the hammer cone, can be adjusted by thumbscrews to give a drop to the hammer varying from a fraction of a millimeter to 10 cm. This rod has a hollow cone at its lower end into which the cone of the hammer head is thrust when the hammer is lifted by the crosshead *(I)*. When the cone of the hammer head is brought into the cone of the adjusting rod the hammer is exactly centered and brought free of the guide rods *(D)*. As the crosshead *(I)* continues to rise, the bolts supporting the hammer, which are tapered at an angle of about 45°, are thrust open by the sloping head of the adjusting cone rod *(P)* releasing the hammer, which falls on a flat-end plunger *(B)* of 1 kg. weight, which is pressed upon the briquette *(O)* by two light spiral springs surrounding the guide rods *(F)*. This plunger *(B)* is bolted to a crosshead *(G)*. A small lever *(J)* holding a brass pencil *(K)* at its free end, is connected with the side of the crosshead, by a link motion arranged so that it gives a vertical movement to the pencil five times as great as the movement of the

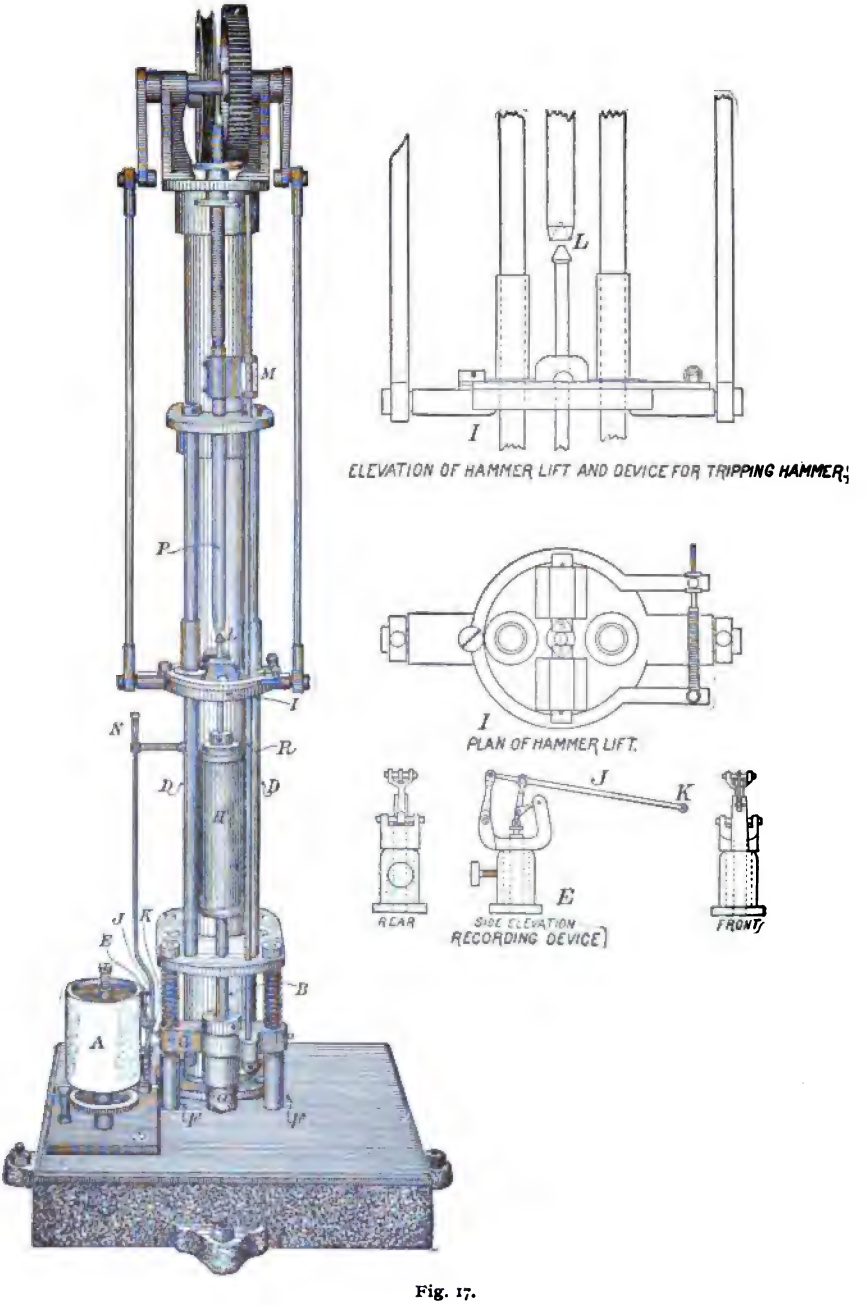

L
I
ELEVATION OF HAMMER LIFT AND DEVICE FOR TRIPPING HAMMER.
M
P
I
N
R
D
D
H
J
K
E
B
A
I
PLAN OF HAMMER LIFT.
J
K
E
REAR
SIDE ELEVATION
RECORDING DEVICE
FRONT

Fig. 17.

crosshead. The pencil is pressed against a drum *(A)*, and its movement is recorded on a slip of silicated paper fastened thereon. The drum is moved automatically through a small angle at each stroke of the hammer; in this way a record is obtained of the movement of the crosshead during and after each blow of the hammer. To the crosshead *(G)* is fastened a steel rod *(R)* which passes up through the crosshead *(I)* and through a piece of metal securely attached to the cone rod *(P)*. At this junction a vernier scale is graduated, by means of which the height of blow of the hammer can be accurately set to 0.1 mm., and by lowering the cone rod until it rests on the hammer cone *(L)* the height of the briquette can also be measured to 0.1 mm.

The standard fall of the hammer for a test is 1 cm. (0.39 inch) and this blow is repeated until the bond of cementation of the material is destroyed. The blow producing failure is easily ascertained, for when the hammer falls on the plunger, if the material beneath it can withstand the blow it recovers; if not, the plunger stays at the point to which it is driven, and in either case the behavior of the test piece is recorded on the drum. The automatic record thus obtained from each briquette is filed for future reference. A copy of one of these records is shown in Fig. 18. The

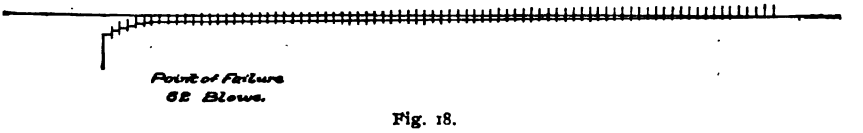


Fig. 18.

number of blows required to destroy the bond of cementation or resilience, as described above, is noted and the average obtained upon five briquettes is given as the cementing value.

The problem of holding the test piece rigidly under the intervening plunger, so that it may not be subjected to lateral movements and transverse strains, is one which has given much difficulty. Until recently a small brass plate with a beveled hole slightly larger than the diameter of the briquette was used, but it was found that the test piece was often seriously abraded by the side thrust developed. Later attempts to secure the briquette by various clamping devices were not satisfactory. Finally the meth-

od was adopted of placing a drop of thick shellac on the bottom of the test piece, which caused it to adhere firmly to the bedplate. Careful attention to such details as these is necessary in order to get satisfactory results from this test.

131. **Method of Heinrich.**—This process consists in mixing the air-dried earth with water until its aqueous content is 50 per cent of the highest water capacity determined by experiment.[67] The sample is next placed between two pieces of sheet iron 10 centimeters square, each of which in its middle point is provided with a hook. The thickness of the layer between the two pieces of iron should be from 5 to 10 centimeters. The exuding particles of soil are cut off with a knife. The upper piece of sheet iron is next suspended by a cord in such a way that the iron piece occupies a horizontal position. A small basket is attached to the lower surface and sand added thereto, little by little, until the column of earth is separated. The sand basket and iron plate are weighed, and the total weight gives the power necessary to separate a column of soil 10 centimeters square in cross section. The iron plates may be roughened so that the adhesion thereto of the soil is greater than its cohesive force.

132. **Adhesion of Soil to Wood, Iron, Etc.**—The adhesive power of moist soil for wood, iron, etc., is measured by Heinrich in the following way: The soil is mixed with water, as above, until it contains just 50 per cent. of its total water-holding content. It is then placed in a large vessel and the upper surface made as smooth as possible. A plate of wood, iron, etc., of 10 centimeters square is then pressed on the surface until a complete contact is secured. This plate, by means of a hook and cord passing over a pulley, is then subjectetd to stress by weighting the cord which carries a basket for that purpose. The basket should be of the same weight as the plate in contact with the soil. The weight added to the basket necessary to separate the plate from the soil is taken to represent the cohesive force. The author of the method appears to take no account of the pressure of the air on the plate caused by the exclusion of the air from its under surface.

133. **Flocculation.**—The union of very fine soil particles to form flocks is a phenomenon of great importance in the mechan-

[67] Grundlagen zur Beurteilung der Ackerkrume, 1882, 226.

ical analysis of soil in which the fine particles are separated in water. This subject will be discussed in part fifth in connection with silt separation.

THE ABSORPTIVE POWER OF SOILS FOR SALTS IN SOLUTION

134. **General Principles.**—It is a fact of every-day observation that soils have a particular property of absorbing certain materials with which they come in contact.[88] If it were not for this property all our wells would soon become unwholesome from the reception of decayed animal and vegetable matter carried to them in the drainage water from the surface. It is also a well-known fact that burying dead bodies prevents the gaseous products of decomposition from reaching and vitiating the atmosphere.

Besides this well-known power of soils to absorb the decomposition products of animal and vegetable matter, they also possess a property which is of far greater importance in plant economy; that is, the power of withdrawing and retaining certain mineral constituents from their solutions. Some theoretical data in relation to this phenenomon will be given in another place.

As far back as the sixteenth century mention is made by Lord Bacon of a process for obtaining pure water on the seashore by simply digging a hole in the sand and allowing it to fill with filtered sea water, which by this means, he alleges, is deprived of its salts. Bacon probably overestimated the power of sand for removing salt from solution but he recognized a property in soils which is of the greatest importance. His general conclusion is, "that ordinary soils possess the power of separating from solution and of retaining for the purposes of vegetation the bases of the different alkaline salts and certain animal and vegetable substances and that this power extends to all those substances to which we attach the chief value as manure." Although certain facts were observed by some of the earlier writers in regard to soil absorption, no systematic researches were conducted with a view of demonstrating the extent and cause of this power until within a comparatively few years.

In 1850 Prof. I. Thomas Way published in the *Journal of the*

[88] Huston and Goss, Purdue University Agricultural Experiment Station, Bulletin, 33, 2 : 46.

Royal Agricultural Society of England, the results of a thorough and most excellent investigation of the subject. The classical researches of Way have served as a basis for all subsequent investigations and in the main the conclusions he reached have been confirmed. Since then many distinguished chemists, such as Henneberg, Stohmann, Peters, Heiden, Knop, Ullik, Pillitz, Biedermann, Tuxen, Hilgard and others have given their attention to this matter.

135. **Summary of Data.**—If a solution of a soluble sulfate, chlorid or nitrate of an alkali or an alkaline-earth metal be placed in contact with a soil, a part of the base is withdrawn but none of the acid. This absorption of base is attended with the liberation of some other base from the soil combining with the acid of the solution. Any alkali or alkaline earth base has the power of replacing any other such base. However, if soluble phosphates and silicates of these bases be placed in contact with the soil both the base and the acid are removed from the solution.

Peters has shown that the amount of absorption depends upon the concentration of the solution, the relation between the quantity of solution and the soil and the kind of salt used.[89] He treated 100 grams of earth with 250 cubic centimeters of solutions of different potash salts with the following results:

Strength of solution.	$\frac{1}{10}$ Normal.	$\frac{1}{20}$ Normal
Salt Used	Grams K_2O absorbed.	Grams K_2O absorbed.
KCl	0.3124	0.1990
K_2SO_4	0.3362	0.2098
K_2CO_3	0.5747	0.3154

Beidermann proves that, for phosphoric acid at least, the absorption increases with the temperature.[90]

It has also been found that the amount of absorption depends upon the time of contact between the soil and solution. Way found that the absorption of ammonia was complete in half an hour, while Henneberg and Stohmann noticed that the phosphoric acid continued to be fixed after the expiration of 24 hours.[91]

[89] Knop, Agricultural Chemistry.

[90] Beiträge zur Frage der Bodenabsorption.

[91] Journal für Landwirtschaft, 1859, New Series, [3], 25.

It is a very important fact that the absorption of a base is never complete; no matter how dilute the solution it will still carry a small portion of the base with it. Peters states that it requires about 28,000 parts of water to remove one part of absorbed potash and Stohmann found that it required about 10,000 parts of water to remove one part of absorbed ammonia. With phosphoric acid, the resulting compound seems to be much more insoluble.

According to Tuxen nitrate of soda and common salt diminish the capacity of the soil to absorb ammonia and potash and increase its capacity to absorb phosphoric acid.[92] Both nitrate of soda and common salt dissolve the potash combined in the soil in larger quantities than water alone.

136. **Cause of Absorption.**—The withdrawing and fixing of phosphoric acid from solutions by the soil is not very difficult to understand as this acid forms insoluble compounds of iron, lime, and magnesium, some or all of which bases are present in all soils. As to the absorption of the alkalies, the explanation is far more difficult as nearly all of their ordinary compounds are readily soluble in water. It appears from researches conducted in the Bureau of Chemistry by Cushman that clay in a colloidal state has the property of dissociating to a certain extent potash salts and entangling the basic ion in the meshes of the colloid structure. For instance, if a solution of potassium chlorid is shaken with clay and poured upon a filter a part of the potash will be missing in the filtrate although all the chlorin passes through.

As lime is usually found combined with the acid part of an alkali salt, from which the base has been absorbed by the soil, it might naturally be supposed that the absorptive power of the soil would depend upon the amount of lime present. Way found, however, that the addition of chalk in no way influenced the absorption of ammonia by a soil which contained but a small amount of lime. This fact was also confirmed by Knop who found that chalk exerted no influence on the absorption of ammonia salts.[93] These facts would seem to point to the conclusion that lime was present in sufficient quantity in these experiments, or that it is not essential to the phenomena of absorption. However, as any

[92] Die Landwirtschaftlichen Versuchs-Stationen, 1882, 27 : 113.

[93] Die Bonitirung der Ackererde, 1871, 49.

alkali or alkaline-earth base can under certain conditions replace any other such base, the presence of lime in the filtrate from a soil treated with water is probably more of an accidental occurrence, owing to the comparatively large amount of that substance in most soils, than a necessary condition, as any other base would doubtless answer the same purpose in the absence of lime.

137. **Warrington** has shown that hydrated oxids of iron and aluminum, and especially the former, are capable of absorbing potash and ammonia, and as more or less of these hydrates exist in nearly all soils, a part, at least, of absorptive phenomena is to be ascribed to them, and this fact seems in harmony with the colloid theroy of absorption mentioned above.[94]

138. **Way** tried to determine which of the constituents of a soil exercised chiefly the absorptive power.[95] He passed a solution of ammonia through tubes containing pure sand and found that it came through apparently unaltered from the first, while a soil treated in the same way removed the ammonia for a considerable time. He concluded from this that the absorptive power does not exist in the sand. He next oxidized the organic matter in a soil with nitric acid and then treated it with ammonia in the same way. The first portion of the filtrate showed no ammonia in any form, hence he concluded that organic matter is not essential to the act of absorption. Clay was shown to have a higher absorptive power before than after burning. This would indicate that the power of absorption is related in some way to the form of the colloid structure. Some kinds of burned clay as powdered clay tobacco pipes, however, are capable of causing absorption phenomena.

Having shown that clay was the main constituent in a soil which caused the absorption of alkalies, he tried next to trace the particular compounds which caused the absorption. Having tried various natural silicates he at last succeeded in producing a hydrated silicate of aluminum and soda which exhibited displacement and absorptive properties very similar to those shown by the soil.

As Way had succeeded in producing an artificial hydrated silicate possessing absorptive properties Eichorn thought of trying

[94] Journal of the Chemical Society, London, 1868, 21.

[95] Journal of the Royal Agricultural Society, 1850, 313-379.

natural hydrated silicates or zeolites and found that they exhibited the same power as Way's artificial preparation.[96] It has also been shown by Beidermann, Rautlenberg,[97] and Heiden[98] that the absorptive power bears a close relation to the amount of soluble silicates present.

In view of these facts it is now generally accepted that the absorption of salts of the alkalies, accompanied by the change of base, is due chiefly to the presence of decomposed zeolite minerals in the soil.

Besides the purely chemical absorption of salts by the soil, we have a physical absorption of various substances similar to the action of charcoal when used as a filter.

139. **Conclusions of Armsby.**—The data connected with the absorption of bases by a soil have also been reviewed by Armsby.[99] He shows that the absorption is accompanied by a chemical reaction between the salt whose base is absorbed and some constituent of the soil, and this change seems to be due particularly to certain zeolite silicates, although Liebig and others are disposed to credit this absorption largely to physical causes.

Knop advances the idea that the soil has the power of disintegrating salts in the presence of some substances like calcium carbonate which can unite with the acid. In experiments made with hydrous silicates it was shown that the absorption resembled in all cases like phenomena in the soil; hence the supposition already advanced in regard to the influence of such silicates is doubtless true.

In respect of absorption in general, the following conclusions are reached:

1. The absorption of combined bases by the soil consists in an exchange of bases between the salt and the hydrous silicates of the soil.

2. This exchange, which is primarily chemical, is only partial, its extent varying;

[96] Landwirtschafliches Central-Blatt, 1858, **2** : 169.

[97] Journal für Landwirtschaft, New Series, 1862, **7** : 49.

[98] Annalen der Landwirtschaft in der Königlich Preussesichen Staaten, **48** : 310.

[99] American Journal of Science, [3] 1877, **14** : 75.

(a) with the concentration of the solution;

(b) with the ratio between the volume of the solution and the quantity of soil used.

3. The cause of these variations is probably the action of mass or the tendency of resulting compounds to reform the original bodies, the absorption actually found in any case marking the point where the two forces are in equilibrium.

140. Selective Absorption of Potash.—As a rule more potash is absorbed from the sulfate than from the chlorid. This fact would seem to point to the advisability of using sulfate as a fertilizer in preference to chlorid. However, as with the exception of nitrates, the absorptive power of a soil for the salts used as fertilizers, is many times greater than it is ever called upon to exert in fixing applied fertilizers, we need not trouble ourselves in regard to the absorption of phosphoric acid, potash or ammonia, in so far as the practical side of the matter is concerned. For example, an acre of soil to the depth of nine inches weighs about 900 tons. Now it has been found by Huston, that 100 parts of a soil experimented upon absorbed over 0.25 part of P_2O_5, hence 900 parts would absorb over 2.25 parts of P_2O_5; or an acre of this soil to the depth of nine inches would absorb over two and one-fourth tons of phosphoric acid.[1] For field crops 500 pounds of a high grade phosphoric fertilizer is often employed containing about 100 pounds of P_2O_5; hence the power of such a soil to absorb phosphoric acid is more than 45 times as great as it is called upon to exert in fixing the phosphoric acid added to it as a fertilizer in such a case.

Huston has further shown that an acre of soil nine inches deep will absorb more than 2.7 tons of potash (K_2O) from potassium chlorid, from which salt less potash is absorbed than from the sulfate. If one-tenth ton of potassium chlorid per acre is an average dressing of potash for field crops, this soil possesses the power of absorbing more than 27 times as much potash as is applied as a fertilizer.

In like manner it may be shown that the power of an acre of soil nine inches deep to absorb ammonia from ammonium sulfate is more than 32 times as great as it would be called upon to exert

[1] Manuscript communication to author.

in fixing the ammonia from a dressing of one-quarter ton of ammonium sulfate per acre.

With sodium nitrate, however, there is no absorption; hence great care is necessary in the application of nitrogen as a nitrate, for, if it be put on in large quantities, at a season when the plant is not prepared to assimilate it, or during a period of heavy rains, there must unavoidably result loss from drainage. The best time to apply a nitrate is evidently during the active growing season.

141. Relation of Absorptive Power to Fertility.—It has been shown by King that there is a direct relation between the fertility of a soil and its power to absorb certain salts.[2] Especially is this true of potash. The absorption of potash in four typical Northern soils in nearly double that of four typical Southern soils. In every case the soil removing the most potash from the solution used gave the largest yield.

142. Effect of Area.—The surface area of soil particles in respect of their power to absorb solutions of salts, is a factor of great importance. The finer the particles of a soil the greater the surface area it presents and consequently the greater surface attraction. The approximate surface area of a cubic foot of each of the different typical soils of Maryland as estimated by Whitney is as follows:[3]

Pine barrens	23,940	square feet.
Garden lands	74,130	" "
Tobacco lands	84,850	" "
Wheat lands	94,540	" "
River terrace	106,260	" "
Limestone subsoil	202,600	" "

It will be seen that there are about 24,000 square feet of surface area in a cubic foot of the subsoil of the pine barrens, no less then 100,000 square feet or two and three-tenths acres of surface area in a cubic foot of the subsoil of the river terrace, and 200,000 square feet of surface area in a cubic foot of the limestone subsoil.

[2] Investigation in soil management, privately published, Madison, Wis., 114.

[3] Maryland Agricultural Experiment Station, Fourth Annual Report, 282.
Bulletin No. 4, Weather Bureau, 14.

These figures seem vast, but they are probably below rather than above the true values, on account of the wide range of the diameters of the clay group. This great extent of surface and of surface attraction, which has been described as potential, gives the soil great power to absorb moisture from the air, and to absorb and hold back mineral matters from solution. A smooth surface of glass will attract and hold, by this surface attraction, an appreciable amount of moisture from the surrounding air. A cubic foot of soil, having 100,000 square feet of surface, should be able to attract and hold a considerably larger amount of moisture.

It might have been added that if the potential of the surface, separating the solution from the soil, be greater than the potential in the interior of the liquid mass, there will be a tendency to concentrate the liquid on this surface of separation. It has been shown that certain fluids have greater density on a surface separating the fluid from a solid. On the other hand, if the potential were low there might be no tendency for this concentration, and even the reverse conditions would prevail and the soluble substance could be readily washed out of the soil.

143. **Theory of Surface Tension.**—The principles on which the phenomena of surface tension in soils are based have been clearly stated by Briggs.[4] These phenomena are due to the action of certain molecular forces. In a drop of liquid the forces acting on a molecule at or near the center may be considered as producing equilibrium, while at or near the surface such is not the case.

144. **Removal of Organic Matters.**—It is probably largely due to this restraining power that organic matters are removed from solutions in percolating through the soil. Organic matter in the soil however is subjected to vigorous attacks by the bacteria with which it comes in contact, which not only destroy the protein matter but also both the soluble and insoluble carbohydrates.

145. **Importance of Soil Absorption.**—The importance of the absorptive power of the soil can hardly be overestimated. By means of this power those mineral ingredients of plant food, of which most soils contain but little, are held too closely to allow of

[4] The Mechanics of Soil Moisture, Bull. 10, Division of Soils, U. S Dept. of Agriculture, 7.

rapid loss by drainage, and still sufficiently available to answer the needs of vegetation, provided the store is large enough. The only important plant food in the soil which does not come under the influence of absorption is nitrogen in the form of salts of nitric acid, and nature has made a wise provision for this element by binding it in the form of insoluble organic bodies which nitrify but slowly, and by supplying each year a small quantity from the atmosphere.

By means of the absorptive power of soils the farmer, if he puts on an excess of potash or phosphoric acid as a fertilizer, does not lose it all but is able to reap some benefits from it in the next and even in succeeding crops. If it were not for this power of the soil in holding any excess of plant food which may be present or added, the best method for applying fertilizers would be a much more complicated problem than it is at present; and it would be necessary to apply them at just the proper season and in nicely regulated amounts to insure against loss.

The general principles which underlie the absorption, retention and release of plant foods in the soil belong to the domain of physical chemistry. The problem of equilibrium in the soil however is a most complicated one, due to the great number of active bodies and the ever varying conditions of temperature, moisture, bacterial activity and plant growth.

146. **Method of Determining Absorption of Chemical Salts.**—The soil which is to be used for this experiment should be treated as has been indicated and passed through a sieve the meshes of which do not exceed half a millimeter in size. From 25 to 50 grams of the fine earth may be used for each experiment.

The fine earth should be placed in a flask with from 100 to 200 cubic centimeters of the one-tenth to one-hundredth normal solution of the substance to be absorbed. The flask should be well shaken and allowed to stand with frequent shaking from 24 to 48 hours at ordinary temperatures. The mixture is then to be thrown upon a folded filter and an aliquot part of the filtrate employed for the estimation, corrected for the amount of water in the soil used. The methods of determining the quantities of the substances used will be found in other parts of this manual. It is recommended to conduct a blank experiment with water under

the same conditions in order to determine the amount of the material under consideration abstracted from the soil by the water alone. The difference in the strength of the solution as filtered from the soil, and the original solution will give the absorptive power of the soil for the particular substance under consideration.

If it should be desired to determine the absorptive power of the soil for all the ordinary chemical fertilizing materials at the same time, a larger quantity of the sample should be employed corresponding to the increased amount of the standard solutions used. About 500 cubic centimeters of the mixed salt solution should be shaken with 125 grams of the earth and the process carried on in general as indicated above. The absorption coefficient of an earth for any given salt according to Fesca, is the quantity of the absorbed material expressed in milligrams calculated to a unit of 100 grams of the soil.[5]

147. **Method of Pillitz and Zalomanoff.**—It is recommended by Pillitz and Zalomanoff to reject the old method, *viz.*, shaking the soil with the solution in a flask, and substitute the filtration method both because it gives a more natural process and because the results are more constant. The apparatus is shown in Fig .19.

Two cylinders are placed vertically, one over the other. The lower cylinder is graduated in cubic centimeters, the upper cylinder is closed at each end by perforated rubber stoppers *a* and *b* through the openings of which the glass tubes *c* and *d* pass. Within the cylinder *a* the opening of the small tube *d* is closed with a disk of Swedish filter paper. The lower part of the small tube *d* is connected by means of a rubber tube carrying a pinch-cock *c* with another small tube *e* which passes through the stopper *f*. In carrying out the process the weighed quantity of soil is placed in the upper cylinder and afterwards the measured quantity of the solution, the whole thoroughly mixed and the cylinder closed. The valve C is then opened, a given quantity of the solution, but not all, is made to drop into the lower cylinder and the valve C is closed. The liquid which has passed into the lower cylinder as well as that which remains in the upper cylinder, is thoroughly

[5] Beiträge zur agronomische Bodenuntersuchung, 31.

stirred and the quantity of the soluble material remaining in both liquids determined and the absorbing power of the soil estimated from their difference. It does not appear that this method of estimation of the absorption power possesses any special advantages over the old and far simpler method of shaking in a flask.

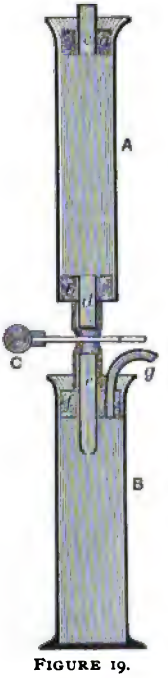


FIGURE 19.

PILLITIZ'S APPARATUS FOR DETERMINING ABSORPTION OF SALTS BY SOILS.

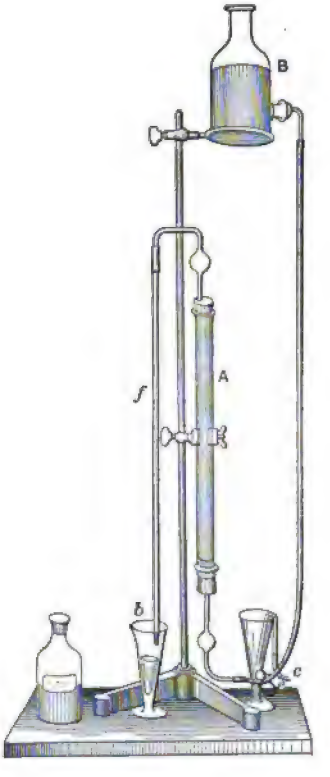


FIGURE 20.

MÜLLER'S APPARATUS TO SHOW ABSORPTION OF SALTS BY SOILS.

148. Method of Muller. — The method of Müller for illustrating absorption is carried out by means of the apparatus shown in Fig. 20. A glass cylinder A about 750 centimeters long and four to five centimeters wide is closed at each end with rubber stoppers with a single perforation.[7] The cylinder A serves for the

[7] Zeitschrift für angewandte Chemie, 1889, **18** : 501.

reception of the soil with which the experiment is to be made. Before using, the lower part of it is filled with glass pearls or broken glass and above this a layer of glass wool is placed about one centimeter thick. The object of this is to prevent the soil from passing into the small tube below. As soon as the soil has all been placed in the cylinder A the upper part of the tube is also filled with glass wool. The cylinder A is connected with the pressure bottle B by means of a rubber tube and the small glass bulb tube shown in the figure. The bottle B should have a content of about two liters. It is filled with the standard solution of the material of which the absorption coefficient is to be determined. At *c* the rubber tube is connected with a glass T, one arm of which is provided with a piece of rubber tubing which can be closed by means of a pinch-cock. At *e* a screw pinch-cock is placed which can be used to regulate the flow of the solution from B to A. By opening the pinch-cock at *c* on the short arm of the T piece, a sample of the original liquid can be removed and this can be compared with the part which runs to *b*. If it is desired for instance, to show that potassium carbonate has been absorbed by the soil the two bulbs shown on the small glass tubes connecting with A can be filled with red litmus paper. This paper will at once be turned blue in the lower bulb while in the upper one it will retain its original color because the liquid in passing through the soil will have lost its alkaline reaction. The solution used should be very dilute. The apparatus is designed particularly for lecture experiments rather than for quantitative determinations.

149. **Method of Knop.**—For rapid determination of the absorption coefficient of the soil Knop's method may be used.[8]

The fine earth which is employed is that which passes a sieve with meshes of half a millimeter. From 50 to 100 grams of this soil are mixed with from five to 10 grams of powdered chalk and with from 100 to 200 cubic centimeters of ammonium chlorid solution of known strength. The ammonia solution should be of such a concentration that the ammonia by its decomposition for each cubic centimeter of the liquid evolves exactly one cubic cen-

[8] Die Bonitierung der Ackererde, Leipzig, 1872, 49.
Wahnschaffe, Anleitung zur wissenschaftlichen Bodenuntersuchung, 133.

timeter of nitrogen. This solution is prepared by dissolving in 208 cubic centimeters of water at 17°.5 one gram of ammonium chlorid. With frequent shaking the solution is allowed to stand in contact with the soil for 48 hours. The whole is now allowed to settle and the supernatant clear liquid is poured through a dry filter. From the filtrate from 20 to 40 cubic centimeters are removed by a pipette, and evaporated to dryness in a small porcelain dish, with the addition of a drop of pure hydrochloric acid. The ammonium chlorid remaining in the porcelain dish is washed with 10 cubic centimeters of water into one of the compartments of the evolution flask of the Knop-Wagner azotometer. It is decomposed with 50 cc. of hypobromite of soda diluted with 200 cc. of water and the nitrogen estimated volumetrically. The hypobromite is prepared by dissolving 100 grams of sodium hydrate in 250 cc. of water and adding to the lye 25 cc. of bromin. The difference between the amount of nitrogen in this material and that of the original will give the amount of absorption exercised by the fine earth. Any of the standard methods of determining nitrogen described especially in the second volume of this work may be used instead of the method just given.

150. **Method of Huston.**—The salt solutions used in the experiments conducted by Huston are sodium phosphate (Na_2HPO_4), potassium chlorid, potassium sulfate, ammonium sulfate and sodium nitrate.[9]

The solutions should be approximately tenth normal, the actual strength in each case being determined by analysis. The phosphorus is determined as magnesium pyrophosphate in the usual way, the potash as potassium platinochlorid, the ammonia by collecting the distillate from soda in half normal hydrochloric acid and titrating with standard alkali, and the nitrate by Warington's modification of Schlösing's method for gas analysis. The details of these methods of determination will be given later. One hundred grams of the sifted, air-dried soil are placed in a rubber-stopped bottle and treated with 250 cc. of the solution to be tested. The digestion is continued for 48 hours in each case, the bottles being thoroughly shaken at the end of 24 hours. At the end of the treatment the solutions are filtered and

[9] Experiment Station, Purdue University, Bulletin 33, 50.

the salts determined in aliquot portions. The details of this method are essentially those already described.

151. **Statement of Results.**—Duplicate analyses should be made and the tabulation of the data is illustrated in the following analyses by Huston:

Na_2HPO_4 cubic centimeters filtrate.	Weight of $Mg_2P_2O_7$ in 25 cubic centimeters of the solution.	Weight of $Mg_2P_2O_7$ in filtrate.	P_2O_5 absorbed by 100 grams soil.	Salt removed per cent.
(a) 25	0.1368 gram	0.0962 gram		
(b) 25		0.0963 "	0.2589 gram	29.6
	Mean	0.0963 "		

KCl cubic centimeters filtrate.	Weight of K_2PtCl_6 in 25 cubic centimeters of solution.	Weight of K_2PtCl_6	K_2O absorbed by 100 grams soil.	Salt removed per cent.
(a) 25	0.6154 gram	0.4505 gram		
(b) 25		0.4540 "	0.3161 gram	26.5
	Mean	0.4523 "		

K_2SO_4 cubic centimeters filtrate.	Weight of K_2PtCl_6 in 25 cubic centimeters of solution.	Weight of K_2PtCl_6	K_2O absorbed by 100 grams soil.	Salt removed per cent.
(a) 25	0.6113 gram	0.4426 gram		
(b) 25		0.4371 "	0.3324 gram	28.0
	Mean	0.4399 "		

$(NH_4)_2SO_4$ cubic centimeters filtrate.	Number of cubic centimeters one-half normal acid neutralized by 50 cubic centimeters of solution.	Cubic centimeters Half normal acid neutralized.	N absorbed by 100 grams soil.	Salt removed per cent.
(a) 50	10.00	7.25		
(b) 50		7.25	0.0964 gram	27.5
	Mean	7.25		

$NaNO_3$ cubic centimeters filtrate	Number cubic centimeters N_2O_3 afforded by 10 cubic centimeters of solution at 0° and 1000 millimeters pressure.	Cubic centimeters N_2O_3 at 0° and 1000 millimeters.	N absorbed by 100 grams soil.	Salt absorbed per cent.
(a) 10	16.63	16.77		
(b) 10		16.70	none	00.00
	Mean	16.73		

Upon comparing the figures it will be found that the absorption, passing from the greatest to the least, is as follows: phosphoric

acid (P_2O_5), potassium sulfate, ammonium sulfate, potassium chlorid and sodium nitrate.

It will be seen that there was no absorption in the case of the nitrate, while with each of the other salts there was quite a marked absorption. It will also be noticed that the percentages of absorption are not very different, and especially is this true of the potassium and ammonium salts, the P_2O_5 being somewhat higher. Whether this fact is merely an accidental occurrence or is due to the law of combination by equivalents could hardly be predicted from the single soil experimented upon; but taking into consideration the possibility of difference in solubility of the resulting compounds in the saline solutions used, and of other varying conditions, the percentages are evidently not far enough apart to exclude the possibility of the bases uniting in equivalent proportions.

152. Preparation of Salts for Absorption.—The salts employed in the determinations of absorption are conveniently prepared in fractional normal strength.

In grams per liter the following quantities are recommended, *viz.*, 5.35 g NH_4Cl; 10.11 g KNO_3; 16.40 g $Ca(NO_3)_2$; 24.60 g $MgSO_4 + 7H_2O$; 2.34 g $CaH_4(PO_4)_2$.

The ammonium chlorid, potassium nitrate and magnesium sulfate can be weighed as chemically pure salts and the standard solution be directly made up. Calcium nitrate is so hygroscopic that a stronger solution must be made up, the calcium determined and the proper volume diluted to one liter.

Monocalcium phosphate is prepared as follows:

A solution of sodium phosphate is treated with glacial acetic acid and precipitated with a solution of calcium chlorid. It is then washed with water until all chlorin is removed. The fresh precipitate is saturated with pure, cold phosphoric acid of known strength. After filtering the solution is placed in a warm room and left for two or three weeks until crystallization takes place.

The crystals are pressed between blotting papers and finally dried over sulfuric acid and washed with water-free ether, and again dried. Since this salt is decomposed in strong solutions it should be used only in one hundredth normal strength, *viz.*, 2.34 grams per liter.

POROSITY AND ITS RELATIONS TO MOISTURE

153. **Porosity.**—The porosity of a soil depends upon the state of divisibility and arrangement of its particles, and upon the amount of interstitial space within the soil. If a soil be cemented together into a homegeneous mass, its porosity sinks to a minimum; if it be composed, however, of numerous fine particles, each preserving its own physical condition, the porosity of the soil will rise to a maximum. The porosity of a soil may be judged very closely by the percentage of fine particles it yields by the process of silt analysis to be described further on. In general, the more finely divided the particles of a soil, the greater its fertility. This arises from various causes; in the first place, such a soil has a high capacity for absorbing moisture and holding it; thus the dangers of excessive rain-falls are diminished, and the evil effects of prolonged drought mitigated. In the second place, a porous soil permits a freer circulation of the gases found in the soil. The influence of lime in securing the proper degree of porosity of a soil is very great, especially in alluvial deposits and other stiff soils. It prevents the impaction which will necessarily follow in a soil which is too finely divided. In general, the porosity of the soil may be said to depend on three factors, *viz.:* 1. Upon the state of divisibility or the number of particles per unit volume; 2. Upon the nature and arrangement of these particles; 3. Upon how much interstitial space there is in the soil.

154. **Influence of Drainage.**—Good underdrainage increases the porosity of a soil by removing the excess of water during wet seasons and rendering the soil more sensitive to capillary attraction which will supply moisture during dry seasons. The influence of tile drainage on the production of floods has been carefully studied by Kedzie, who shows that surface ditching in conjunction with deforesting may increase floods and contribute to droughts, and that tile-drainage may increase flood at the break-up in spring, when the water accumulated in the surface soil by the joint action of frost and soil capillarity during the winter, and the surface accumulations in the form of snow are suddenly set free by a rapid thaw.[10]

[10] Proceedings of the Ninth Meeting of the Society for the promotion of Agricultural Science, 1888, 46.

He also points out that during the warm months tile-draining tends to prevent flood by enabling the soil to take up the excessive rain-fall and hold it in capillary form, keeping back the sudden flow that would pass over the surface of the soil if not absorbed by it, and it mitigates summer drought by increased capacity of the soil to hold water in capillary form and to draw upon the subsoil water supply.

155. **Soil Moisture.**—The capacity of a soil to absorb moisture and retain it depends on its porosity and is an important characteristic in relation to its agricultural value.

The following general principles relating to soil moisture are adapted from Stockbridge.[11]

During dry weather plants require a soil which is absorptive and retentive of atmospheric moisture. The amount of this retention is generally in direct ratio to two factors, *viz.*, the amount of organic matter and its state of division. The capillary water of the soil is very closely related to its percolating power, since all waters in the soil are governed in their movements by what is known as capillary force. Liebenberg has shown that this movement may be either upwards or downwards, according as the atmosphere is dry or supplies soil-saturating rain. The water absorbed by the roots passes into the plant circulation, and the greater part is evaporated from the leaves. Where the supply of water is insufficient, the plant wilts, and if the evaporation long continue in excess of the supply obtained from the soil, the plant must die. The experiments of Hellriegel have shown that any soil can supply plants with all the water they need, and as fast as they need it, so long as the moisture within the soil is not reduced below one-third of the whole amount that it can hold. The quantity of water required and evaporated by different agricultural plants during the period of growth has been found to be as follows:

One acre of wheat	exhales	409,832	pounds of water.		
" " " clover	"	1,096,234	"	"	"
" " " sunflowers	"	12,585,994	"	"	"
" " " cabbage	"	5,049,194	"	"	"
" " " grape-vines	"	730,733	"	"	"
" " " hops	"	4,445,021	"	"	"

[11] Rocks and Soils, 155.

Dietrich estimates the amount of water exhaled by the foliage of plants to be from 250 to 400 times the weight of dry organic matter formed during the same time. Cultivation conserves soil moisture. It must be remembered that this water contains soil ingredients in solution. Hoffmann has estimated that the quantity of matter dissolved from the soil by water varies from 0.242 to 0.0205 per cent. of the dried earth. The experiments of Humphrey and Abbott have shown that a large part of the total sediment of the Mississippi river is soluble in water.

156. States of Water in Soil.—The water in the soil may be regarded as capable of movement and fixed. Any amount of water in the soil which is above that required for saturation is subject to the law of gravitation and tends to disappear by drainage. The quantity of water necessary to saturate a soil is that which is held in place by the attractions which are equal in magnitude to the attraction of gravity.

Whenever there is less water than the above amount capillary movement tends to distribute the rest so as to restore equilibrium, that is capillary movement is towards the driest part. Water which is not affected either by gravitation or capillary movement is fixed in its position by surface tension.

157. Surface Tension.—The force with which a liquid film attaches itself to a solid surface is a modification of molecular force known as surface tension. The nature and purity of the surface modify the surface tension. The presence of dissolved matters in the liquid also greatly modify the degree of attraction. Mercury in general exhibits the highest surface tension of bodies liquid at ordinary temperatures and water is next in order.

The water in soils is never pure but is always contaminated with a greater or less amount of organic and mineral matter in solution. Aqueous solutions of salts usually show a higher surface tension than water. Potash is a substance quite invariably found in soil waters. The following table given by Briggs shows the variations produced in surface tension by the kinds of potash salts and under the conditions of concentration specified.[12] The dyne measures the attraction between two gram masses at a distance of

[12] Mechanics of Soil Moisture Bulletin No. 10, Division of Soils.

1 cm. apart (from center to center) or in other words $^1/_{980}$ of the force of gravitation on one gram mass.

SURFACE TENSION OF SOLUTIONS OF SALTS IN WATER.

Salt in solution	Density.	Concentration.[a]	Temperature. °C.	Surface tension. *Dynes per cm.*
KCl	1.170	25	15–16	82.8
KCl	1.101	15	15–16	80.1
KCl	1.046	7	15–16	78.2
NaCl	1.193	25	20	85.8
NaCl	1.107	15	20	80.5
NaCl	1.036	5	20	77.6
K_2CO_3	1.357	35	15–16	90.9
K_2CO_3	1.157	16	15–16	81.8
K_2CO_3	1.040	5	15–16	77.5
KNO_3	1.126	19	14	78.9
KNO_3	1.047	7	14	77.6
$MgSO_4$	1.274	24	15–16	83.2
$MgSO_4$	1.068	6	15–16	77.8

a. Approximate weight of the dissolved substance in 100 parts by weight of the solution

Briggs adds the observation that most organic substances found in soils, especially those of an oily nature, being insoluble in water and hence most evident on the surface, lower the surface tension to a marked degree. The tension of soil extracts, therefore, is generally much lower than that of pure water, in spite of the presence of dissolved salts.

158. Determination of the Porosity of the Soil.—The porosity of the soil is fixed by the relative volume of the solid particles as compared with the interstitial space. It is most easily determined by dividing the apparent by the real specific gravity.

Let the real specific gravity of a soil be 2.5445 and the apparent specific gravity of the same soil be 1.0990.

The porosity is then calculated according to the following ratios, *viz.:*

$$2.5445 : 1.099 = 100 : x$$

Whence $x = 43.2 =$ per cent. volume occupied by the solid particles of the soil.

The per cent. volume occupied by the interstitial space is therefore 56.8.

159. Volume of Interstitial Space.—The total volume of interstitial space within the soil, in which water and air can enter, is determined by calculation from the specific gravity and the weight of a known volume of soil.[13] For this purpose the soil is sampled

[13] Whitney, Weather Bureau Bulletin 4, 23.

in the following way: A brass tube, about two inches in diameter and nine inches long, has a clock spring securely soldered into one end, and this end turned off in a lathe to give a good cutting edge of steel. The area enclosed by this steel edge is accurately determined, and a mark is placed on the side of the tube exactly 15 centimeters from the cutting edge. A steel cap fits on top of the brass cylinder to receive the blows of a heavy hammer or wooden mallet. The cylinder is driven into the ground until the six-inch mark is just level with the surface. The whole is then dug out, slipping a broad piece of steel under the cylinder before it is removed, so as to prevent the soil which it contains from falling out. The cylinder is then carefully laid over on its side, and the soil is cut off flush with the cutting edge of steel. The soil is removed from the cylinder, carried to the laboratory and properly dried and weighed. The object of the steel inserted in one end of the cylinder is to reduce the friction on the inside of the tube to a minimum, and thus prevent the soil inside the cylinder being forced down below the level of the surrounding earth. The volume of the soil removed with this sampler can readily be determined by calculation, as the area of the end of the tube is known and the sample is 15 centimeters deep. In a sampler, such as described here, this volume is about 300 cubic centimeters. From the weight of soil and the volume of the sample, the volume of interstitial space may be found by the following formula:

$$S = \frac{\left(V - \frac{W}{\omega}\right) \times 100}{V}$$

S is the per cent. by volume of interstitial space, V is the volume of the tube in cubic centimeters, W is the weight of soil in grams, and ω is the specific gravity of the soil. The specific gravity can be determined for each soil, or the factor 2.65 can be used, which is sufficiently accurate for most work.

The per cent. by volume of interstitial space in the undisturbed subsoil is found to range from about 35 for sandy land, to 65 or 70 for stiff clay lands.

For the determination of the amount of water an air-

dried soil will hold, if all the space within it is completely filled with water, an eight-inch straight Argand lamp chimney, with a diameter of about two inches, can be conveniently used. A mark is placed on the side of the tube, six inches from one end, and the volume of the tube up to this mark is found by covering the end with a piece of thin rubber cloth, or by pressing the chimney down firmly on a glass plate, and making a water-tight joint with paraffin or wax. Water is then poured into the tube up to the six-inch mark, and the weight or volume of water determined. The tube can then be dried, a piece of muslin tied tightly over the top and the whole then weighed. Soil is carefully poured in and the tube gently tapped on a soft support until the soil is six inches deep in the tube, and has the desired degree of compactness. The weight and volume of the soil can thus be determined, and the volume of the interstitial space got from the formula already given. This can also be determined directly by introducing water from above, or by immersing the cylinder of soil up to the six-inch mark in water, and allowing the water to enter the soil from below. With such a short depth of soil, very little water will flow out when the cylinder is suspended in the air. The amount which will flow out when the cylinder is thus suspended, will depend both upon the texture and the depth of soil. It is impossible, however, by this method, to completely remove the air or to completely fill the space within the soil with water; for as the water enters the soil, a considerable amount of air becomes entangled in the capillary spaces, and this could not be removed except by boiling and vigorous stirring, which would altogether change the texture of the soil. The amount of water held by the soil, or the amount of space within the soil into which water and air can enter, will evidently depend upon the compactness of the soil, and this is best expressed in per cent. by volume of space.

160. Porosity of Soil to Air.—King has proposed to gauge the porosity of the soil and thus its relations to the passage of water by its porosity to air.[14]

To this end the rate at which air at a given temperature and

[14] Fifteenth Annual Report Experiment Station of Wisconsin, 1897, 123. Bull. 24, Bureau of Soils, 28.

under a given pressure passes through a column of given length of air-dried soil is determined. The apparatus employed is shown

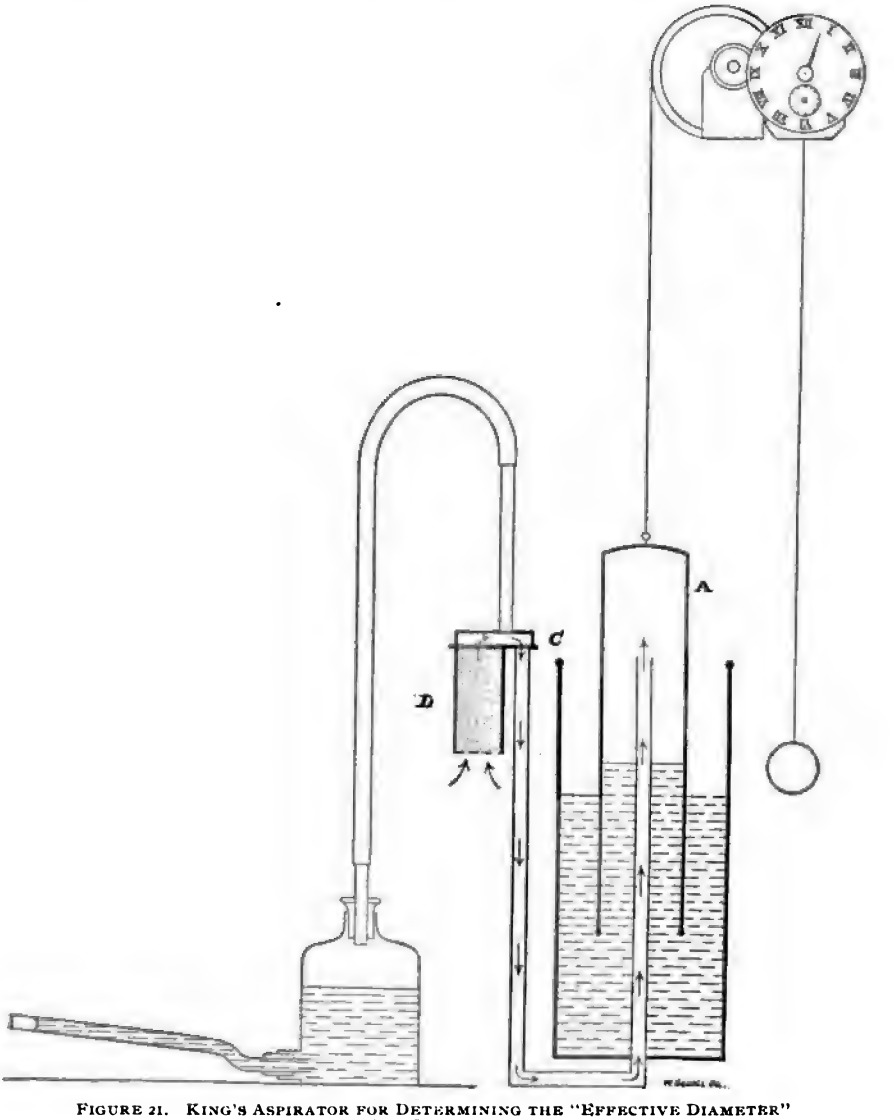


FIGURE 21. KING'S ASPIRATOR FOR DETERMINING THE "EFFECTIVE DIAMETER" OF SOIL PARTICLES.

in Fig. 21. The air-dried previously pestled soil is contained in the

tube D which has a capacity of from 100 to 200 cc. The aspirator A is an elongated gas meter attached to a pulley by a cord as indicated in the drawing. An air meter with index is geared to the aspirator. A water gauge capable of being read to 1 mm. is attached to the air chamber of the apparatus.

In filling the soil tube a light cap is attached to the lower end whihc is closed also with a fine rubber gauze. The finely divided soil sample is introduced in small quantities and gently tamped with a flat pestle until full. The tube is then firmly held against a solid body and struck repeatedly with a light hammer until no further settling takes place, meanwhile being kept quite full. The detachable solid bottom of the tube is then removed and the aspiration performed. The quantity of air passing is expressed in terms of "effective diameter" that is the diameter of a soil composed of spherical particles of the same size and lying as closely together as possible without compression, and which would have the same degree of permeability to air as the sample subjected to experiment. This diameter is computed by a formula constructed by Schlichter, which is as follows:[15]

$$d_2 = .878\frac{hk}{spt}$$

where

d = diameter of grain in cm.
h = length of soil column in cm.
s = area of cross section of soil column in sq. cm.
p = pressure in cm. of water at 20° C.
t = time in sec. for 5,000 cc. of air to flow through at a temperature of 20° C.

The value of k is determined from the following table, being dependent upon the pore space, which must be measured independently.

Per cent. of pore space.	Log. k.	Per cent. of pore space.	Log. k.
26	1,9258	37	1,4173
27	1,8695	38	1,3816
28	1,8195	39	1,3445
29	1,7701	40	1,3078
30	1,7199	41	1,2725
31	1,6732	42	1,2374
32	1,6277	43	1,2024
33	1,5847	44	1,1690
34	1,5409	45	1,1370
35	1,4999	46	1,1058
36	1,4592	47	1,0729

[15] Nineteenth Annual Report U. S. Geological Survey, Part II., 1897-8, 301.
Water Supply and Irrigation Papers, No. 67 U. S. Geological Survey, 1902.

161. Capacity of the Soil for Water.—The soil, as it is taken from the field, may have quite a different water coefficient from the same soil after it has been passed through a fine sieve or been dried at air temperatures or at 100° or 110.° The method of determination which depends upon adding excess of water to a given weight of fine earth, and afterwards eliminating the excess by percolation or filtration, is apt to give misleading results. If, however, the results are obtained by working on the same weight of soil, and in the same conditions, they may have value in a comparative way. The comparison between soils must be made with equal weights, in like apparatus and with the same manipulation, to have any value. These determinations, however, cannot have the same practical value as those made in the samples in a natural condition as has just been described.

162. Method of Wolff Modified by Wahnschaffe.—A cylindrical zinc tube, 16 centimeters long and four centimeters internal diameter, is used, the cubical capacity of which is 200 cubic centimeters.[16]

The cylinder is graduated by placing the moist linen disk on the gauze and tying a piece of rubber cloth over the bottom. Water is poured in until the level is even with the gauze bottom. Add then exactly 200 cubic centimeters of water, mark its surface on the zinc, throw out the water, and file the zinc cylinder down to the mark.

The bottom of the tube is closed with a fine nickel-wire gauze. Below this a piece of zinc tubing of the size of the main tube, pierced laterally with a number of holes, is soldered.

Before using, the gauze bottom of the cylinder is covered with a moist, close fitting linen disk, and the whole apparatus weighed. It is then filled with the fine earth, little by little, jolting the cylinder on a soft substance after each addition of soil to secure an even filling. When filled even full the whole is weighed, the increase in weight giving the weight of soil.

A large number of cylinders can be filled at once and placed in a large crystallizing dish containing water and covered with a bell

[16] Anleitung zur wissenschaftlichen Bodenunterschung, Second Edition, 162.

FIGURE 22.
CAPACITY OF THE FINE SOIL FOR HOLDING MOISTURE. APPARATUS USED IN BUREAU OF CHEMISTRY..

jar. (Fig. 22). The water should cover the gauze bottoms of the cylinders to the depth of from 5 to 10 millimeters. More water should be added from time to time as absorption takes place. The cylinders should be left in the water until when weighed at intervals of an hour no appreciable increase in weight takes place. The temperature and barometer reading should be noted in connection with each determination. With increasing temperature the coefficient of absorption is diminished.

The method of Wolff, as practiced in the laboratory of the Bureau of Chemistry of the U. S. Department of Agriculture, has given very concordant results. Five determinations made on a sample of vegetable soil with the Wolff cylinders, which were weighed at intervals of 10, 20 and 30 days, gave the following results:

No. 1.	Water absorbed after 10 days	106.25	per cent.
" 2.	" " " " "	105.68	" "
" 3.	" " " " "	105.86	" "
" 4.	" " " " "	106.11	" "
" 5.	" " " " "	105.83	" "
	Mean	105.95	" "
No. 1.	Water absorbed after 20 days	106.44	per cent.
" 2.	" " " " "	105.98	" "
" 3.	" " " " "	106.56	" "
" 4.	" " " " "	106.52	" "
" 5.	" " " " "	106.38	" "
	Mean	106.38	" "
No. 1.	Water absorbed after 30 days	108.35	per cent.
" 2.	" " " " "	107.60	" "
" 3.	" " " " "	108.32	" "
" 4.	" " " " "	107.86	" "
" 5.	" " " " "	107.87	" "
	Mean	108.00	" "

The data obtained show that there was only a slight increase in the amount of moisture absorbed after the tenth day.

As will be seen, however, from the following data, the soil within the cylinder does not contain in all parts the same percentage of moisture, the lower portions of the cylinder containing notably larger proportions than the upper parts. The cylindrical soil col-

umn was divided into four equal parts and the moisture determined in each part. Beginning with the top quarter the percentages of moisture are as follows:

First quarter	97.52 per cent.
Second "	105.91 " "
Third "	112.83 " "
Fourth "	116.48 " "

163. **Method of Petermann.**—The method of Wolff as practiced by the Belgin Experiment Station, at Gembloux, is essentially the same as described above.[17]

Peterman recommends the use of tared cylinders from 20 to 25 centimeters long and from six to eight centimeters in diameter. The cylinder is to be filled with the fine earth, little by little, with gentle tapping after each addition. The bottom of the cylinder is closed with a perforated rubber stopper on which is spread a moistened disk of linen. The cylinder, thus prepared and filled, is weighed and afterwards placed in a vessel containing distilled water, to such a depth as to secure a water level about two centimeters above the lower surface of the soil in the cylinder. The level of the water is kept constant as the contents of the cylinder are moistened by capillarity. When the earth appears to be thoroughly moistened, as can be told by the appearance of the upper surface, maintain the contact with water for about five or six hours.

The cylinder is then removed, the upper surface covered to avoid evaporation, allowed to drain for a few hours, wiped and weighed. The cylinder is again placed in water to see if any increase in weight takes place. The weight of the fine earth and of the absorbed water being known, the percentage of absorption is easily calculated.

164. **Method of A. Mayer.**—A glass tube, one and seven-tenths centimeters in diameter, composed of two pieces, 75 centimeters and 25 centimeters in length, is united by a piece of rubber tubing.[18] The lower free end of the 75 centimeter piece is closed with a piece of linen. The tube is filled, with

[17] Analyse du Sol, 13.

[18] Landwirtschaftliche Jahrbücher, 8 : 771.

gentle jolting, with fine earth, the earth column thus extending 25 centimeters above the point of union of the two pieces. Thus prepared, a quantity of water is poured into the upper tube sufficient to temporarily saturate the whole of the soil in the short part of the tube.

During the sinking of the water in the tube there is thus effected a moistening of the material before it is wholly filled with water. After waiting until the free water poured on the top has disappeared the tube is separated at the rubber tube connection and a sample of the moist soil removed at that point. This is at once weighed and then dried at 100°. The loss in weight gives the water absorbed.

The number thus obtained is calculated to the standard by volume, by use of the number representing the apparent specific gravity of the fine earth.

For sand of different degrees of fineness the following numbers were found:

Degree of fineness	2	3	4
Per cent. water absorbed	7.0	13.7	44.6

The numbers thus obtained are taken to represent the absolute water capacity of a mineral substance in powder.

The full water capacity, *i. e.*, the power of holding water when the powder is immersed in water, the excess of which is then allowed to flow away is much greater than the absolute number.

This difference is shown in the following data:

	Quartz, size three.	Clay, size three.
Full water capacity	49.0 per cent.	46.8 per cent.
Absolute water capacity	13.7 " "	24.5 " "

In general the absolute is markedly inferior to the full water capacity. Only in the finest dust do the two numbers approach each other.

165. Volumetric Determination.—A convenient apparatus for this determination has been devised by Fuelling, formerly of the Chemical Division, Department of Agriculture. It is shown in Fig. 23.

It consists of an ordinary percolator the diameter of which decreases slightly towards the lower end, a thick-wall rubber tube

and an ordinary burette, divided in tenths. A rubber stopper is fitted to the mouth of the percolator and perforated twice, in the middle and at the side, the former for a small tube provided with

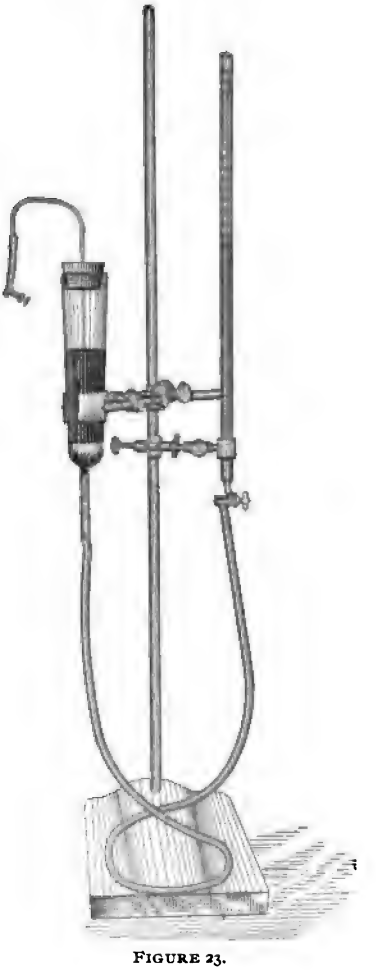


FIGURE 23.
FEULLING'S APPARATUS.

pinch-cock and the latter for the neck of a small funnel. The whole is supported on a convenient stand, the clamp holding the percolator being placed above that supporting the burette, both clamps arranged to slide on the stand-rod.

The method of manipulation is as follows:

A mark is placed upon the projecting tube at the lower end of the percolator, and the tube at this point may be drawn out sufficiently to decrease the width of meniscus to one-eighth inch. Into the percolator is first introduced a small disk of wire gauze or perforated porcelain. Fine shot No. 20 is poured into the percolator to the depth of 2 centimeters and then an equal depth of fine sand which has been previously digested with hydrochloric acid and well cleaned of dust by washing. Through the rubber stopper a small glass tube is passed and its lower end pressed firmly upon the gauze or porcelain disk, its upper end being curved and supplied with a pinch-cock.

The zero.—After the shot and sand have been shaken even, the burette is filled with water and raised above the level of the sand, wetting the percolator for four inches of its length. The burette is lowered and the shot and sand bed allowed to drain by opening the pinch-cock of the inner tube. The burette is raised and the shot-sand flooded repeatedly until, by lowering the burette until the zero mark of the percolator tube is reached, a uniform reading on the burette is secured. Thus the shot-sand bed is completely charged with water. The water level is now made zero on the percolator stem, the burette filled to its zero mark and the apparatus is prepared for the introduction of the soil.

The Determination.—The burette is raised until the water level is three inches above the sand, and the soil gently dropped through a funnel into the water. When the soil has been introduced and wetted completely the water level is raised above the soil and allowed to remain thus two hours. The burette is then lowered and the water allowed to drain from the wetted soil. From four to six hours are usually given for draining. The reading is taken on the burette after establishing the zero on the percolator stem, and the volume of absorbed water thus ascertained.

Example:

Water required to saturate disk, etc	1.50 cubic centimeters.
Weight of air-dried soil	20.00 grams.
Moisture at 105° therein	14.25 per cent.
Weight of dry soil	17.15 grams.
Weight of water in soil	2.85 grams.

Reading of burette after saturation..... 10.75 cubic centimeters.
Deduct water required for disk, etc., 1.50..... 9.25 " "
Temperature..... 20°.00
Deduct weight of 9.25 cubic centimeters H_2O at 20°..... 9.22 grams
Per cent. of water retained by soil..... 70.37
Weight " " " " " ..... 12.07. grams

For general analytical work the correction for variations in the weight of water for different temperatures is of no practical importance. It is better to use the soil in the air-dried state and determine the water therein in a separate portion. Heating a soil to 105° materially alters its texture and the solubility of some of its constituents.

166. **Accuracy of Results.**—A sample of soil from the beet sugar station, in Nebraska, gave the following duplicate results:

First trial..... 45.75 per cent. water.
Second trial..... 44.85 " " "

Vegetable soils from Florida, containing varying proportions of sand, gave the following numbers for duplicate determinations:

Soil No.	First Trial.	Second Trial.
1	144.85 per cent.	145.43 per cent.
2	109.13 " "	107.93 " "
3*a*	46.86 " "	46.51 " "

a very sandy.

167. **Method of Wollny.**—A glass tube is made of a series of separate tubes properly joined together.[19] Each tube is 15 centimeters long and four centimeters internal diameter and carries at each end a short cemented metal end piece having a flattened rim 1.5 centimeters broad. The single tubes are joined together by clamps. The lower end of the tube is closed with a strong piece of coarse linen. The soil to be examined is then filled in little by little, with gentle tamping.

On the upper end two glass tubes are placed, each ten centimeters long and four centimeters internal diameter. These tubes are furnished at each end with cemented brass cylinders which are expanded to a circular, evenly ground rim, 1.5 centimeters wide, also at right angles to the axis of the main tube. These

[19] Forschungen auf dem Gebiete der Agricultur-Physik, 1885, 186.

rims are greased and placed together, one on the other, and held together by wooden clamps.

The short glass tube in immediate connection with the main tube is also firmly filled with the soil sample to the depth of 4 centimeters, so that any settling which may take place in the soil on the addition of water may still find the main glass tube full of the sample. The volume of each of the component tubes before beginning the experiment is measured by the volume of water it contains.

The empty part of the upper glass tube is now filled with water and additional quantities of water are added from time to time until the soil is saturated. The lower end of the main tube is set on a glass plate to prevent evaporation.

As soon as the water shows itself at the lower end of the main tube, the excess of water in the upper glass tube is at once removed by a pipette and a stopper inserted through which a glass tube passes drawn out into a fine point above. The object of this is to avoid evaporation on the upper surface. The apparatus is then left at rest 36 hours. During this time which is necessary in order that all the excess of water may be removed by drainage, loss from evaporation may occur if the upper end of the tube be left open. To avoid this a stopper with capillary opening should be inserted. A tight stopper is not advisable by reason of the partial vacuum which would be formed by the flow of water.

At the end of this time the clamps are removed and the column of moist earth cut with a piece of platinum foil, and the two ends of each separated tube covered with glass plates. It is then weighed and the weight of moist earth determined by deducting the weight of the tube and its glass covers. The moist earth is carefully removed to a large porcelain dish and dried at 100°. After weighing the sample it is allowed to stand 24 hours in the air and reweighed to determine the moisture carried in the air-dry state. The data obtained may also be used to calculate the water content to volume per cent. since the volume occupied by the soil is known from the calibration of the tube. It is shown by these experiments that the water content in soil under the condi-

tions of time and drainage described increases from top to bottom. The difference between the water content of the upper and lower portions is less as the soil particles are finer. The quantity of water which a given volume of soil retains increases with the fineness of the particles.

168. **Method of Heinrich.**—The soil to the depth turned by the plow is dug out and in the hole a thin lead cylinder without bottom, 20 centimeters in diameter and 40 centimeters high, is placed.[20] The soil is then thrown back around and outside the cylinder until the latter appears buried in the ground.

The rest of the soil is passed into the vessel, through a sieve having four meshes to the centimeter, using for this purpose enough water to thoroughly moisten it. Care should be taken not to use enough water to cause any separation of the fine from the coarse particles.

By this process all coarse stones, sticks, etc., are separated. In sandy soils the cylinder is left for a few hours while in clay soils a much longer time is necessary. When the excess of water has disappeared the cylinder is removed, and a disk cut out of the center of it and dried at 100.°

169. **Effect of Pressure on Water Capacity.**—The decreasing capacity of soil to hold water developed by shaking or pressure, is determined by Henrici in the following way:[21]

Into a glass cylinder of 20 millimeters internal diameter are poured 20 cubic centimeters of water. A given quantity of soil is next added, and after standing until thoroughly saturated, the residual water is measured by pouring off, or better, by graduations on the side of the tube. The increase in the volume of the clear water is also measured, after shaking, in the same way. The data of a determination made as above described follow:

Water in cylinder.....	30	cubic	centimeters.
Water and saturated soil	40	"	"
Volume of unsaturated soil $= e =$	10	"	"
Volume of saturated soil $= e + w =$	20.5	"	"
Water contained therein $= w =$	10.5	"	"

[20] Forschungen auf dem Gebiete der Agricultur-Physik, 1885, 259.
[21] Poggendorf's Annalen, **129** : 437.

By repeated shaking the volume of $e + w$, the content of w therein, and the relative values of $\frac{e}{w}$ were found to be as follows;

	Cubic centimeters.	Cubic centimeters.	Cubic centimeters.	Cubic centimeters.
$e + w$	20.5	16.0	15.7	15.0
w	10.5	6.0	5.7	5.0
$\frac{w}{e}$	1.05	0.60	0.57	0.50

If e' represent the volume of the saturated soil then $e' = e + w$, and this gives the relation to the volume of dry earth represented by the equation $\frac{e'}{e} = 1 + \frac{w}{e}$. This indicates that the relative volume of the saturated soil is equal to unity increased by the relative content of water.

170. **Coefficient of Evaporation.**—At an ordinary room temperature in the shade, samples of soil, if they are subjected to examination in tolerably thin layers have nearly an equal coefficient of evaporation. That is, the absolute quantity of water evaporated in a given time is almost entirely conditioned upon the magnitude of the surface exposed and the temperature and saturation of the surrounding air. Only when exposed in conditions as nearly as possible natural in thin layers to the alternate action of the sunlight and shade do the soils show their peculiarities in respect of the evaporation of moisture. In order to ascertain these peculiarities, samples of soil which have been previously examined must be subjected to re-examination at the same time with the soil whose properties are to be determined.

A zinc box is used which should be protected with a well-fitting cover of thick paper, and the different samples of soil which are to be tested placed therein. This should now be placed in a wooden box, the top of which is exactly even with the top of the zinc vessel. This box containing the vessel is exposed to the sunlight. After 24 hours the zinc box can be taken away and its loss in moisture determined, and these weighings, according to the condition of the atmosphere, can be con-

tinued from 14 days to 3 weeks, the temperature of the air of course being carefully determined at each time. At first, all of the different soils being saturated with moisture, it will be observed that the loss of moisture is proportionately the same for all. Soon, however, the rapidity of the evaporation in the samples of soil rich in humus and clay will be decreased as compared with the sandy soils, and in general, those which possess a high capillary power capable of bringing the moisture rapidly from the deeper layers to the surface. There soon comes a point when the difference in evaporation is at its greatest; and then there will be a gradual diminution until the samples lose no further moisture. This point, for the different soils, can be determined by frequent weighings of the vessel.

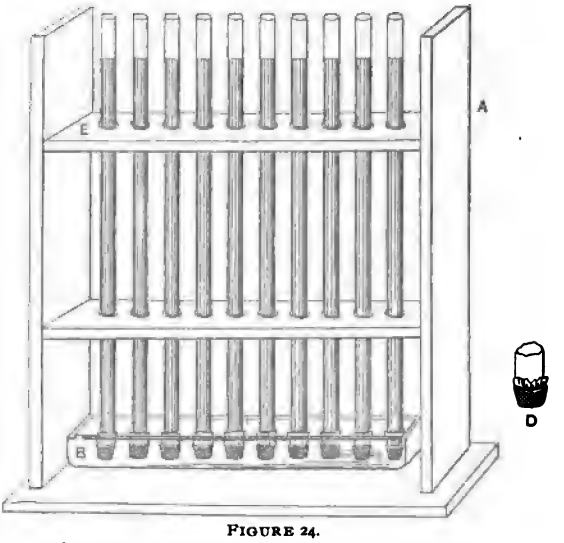


FIGURE 24.
APPARATUS TO SHOW CAPILLARY ATTRACTION OF SOILS FOR WATER.

171. Determination of Capillary Attraction.—Long glass tubes graduated in centimeters may be used for this determination, or plain tubes so arranged as to admit of easy measurements with a rule. The tubes may be from one to two centimeters internal diameter and about one meter long. The fine earth should be evenly filled in little by little, with gentle jolting. The lower end

of each tube, before filling, is closed with a piece of linen, which is held in place by a rubber ring, as shown in D Fig. 24.

The tubes, after filling, are supported in an upright position by a frame AE, in a vessel B containing water in which the linen covered ends D dip to the depth of two centimeters.[22] The height of the water in the several tubes should be read or measured at stated intervals. The water contained in the supply vessel should be kept at a constant height by a Mariotte bottle.

The observations may be discontinued after 24 hours, but even then the water will not have reached its maximum height.

It is recommended by some experimenters to cut the tubes after the above determination is completed, into pieces 10 centimeters in length, and to determine the per cent. of water in each portion.

172. **Statement of Results.**—The following table illustrates a convenient method of tabulating the observed data as given by König:[23]

Number of sample.....		1	2	3	4	5	6	
	24 hours.	27.3	38.0	16.7	36.3	8.0	28.8	centimeters.
Height of	48 "	35.9	50.8	24.6	49.2	11.9	40.5	"
moisture col-	72 "	41.5	59.5	30.0	57.9	15.2	49.1	"
umn after:	96 "	44.4	66.2	33.5	63.8	17.5	55.2	"
	120 "	46.7	70.0	36.3	68.5	19.2	60.5	"

173. **Descending Capillarity.**—In tubes filled with fine earth, as described above, water is quickly poured, the same quantity into each tube of the same diameter, or such quantities in tubes of different diameters as would form a water column of the same depth over the surface of the sample. The rate at which the water column descends in each tube, the time of the disappearance of the water at the surface and the final depth to which it reaches, are the data to be entered.

174. **Statement of Results.**—The points to be observed in the determination of descending capillarity are the number of hours required for the total absorption of a column of water of a given height, the depth of the moisture column at that moment, and the

[22] Wahnschaffe, Anleitung zur Wissenschaftlichen Bodenuntersuchung, 143.

[23] Untersuchung landwirtschaftlich und gewerblich Wichtiger Stoffe, Second Edition, 56.

total depth to which the moisture column finally reaches. The data of observations with six samples with a water column four centimeters high are given by König as follows:[24]

Number of sample.....	1	2	3	4	5	6	
Number of hours required for water to disappear...	4.3	1.8	10.0	3.9	21.0	4.3	
Depth of moisture at time of disappearance of water	11.0	12.0	11.4	13.3	11.7	12.0	centimeters.
Total depth of moisture....	13.0	18.1	13.0	19.0	12.0	16.5	"

175. **Determination of the Coefficient of Evaporation.**—The coefficient of evaporation is the number of milligrams of water evaporated from a square centimeter of soil surface in a given unit of time. It is evident that this number will vary with the physical state of the soil, the velocity of the wind, the saturation of the air with aqueous vapor and the temperature. In all statements of analyses these factors should appear.

The process may be carried on first (a) with soil samples kept continually saturated with water and (b) with samples in which the water is allowed to gradually dry out.

Method a.—The determination may be made in the shade or sunlight.

In the Shade.—A zinc cylinder (Z, Fig. 25), 15 centimeters in diameter and 7.5 centimeters high, with a rim one centimeter wide and one centimeter from top, is covered at one end with linen or octton cloth and filled with fine earth, with gentle jolting, until even with the top. It is then placed in a zinc holder H, into the circular opening of which it snugly fits as in A. This holder is 20 centimeters in diameter and 7.5 centimeters deep. It has an opening at O through which water can be added until it is filled so as to wet the bottom of Z when in place. As the water is absorbed by the soil more is added and, the top being covered, the apparatus is allowed to stand for 24 hours. At the end of this time the soil in the zinc cylinder is saturated with water to the fullest capillary extent.

The whole apparatus, after putting a stopper in O, is now weighed on a large analytical balance and placed in an open

[24] Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe Second Edition, 57.

A

H Z

FIGURE 25.

APPARATUS FOR DETERMINING COEFFICIENT OF EVAPORATION.

room, with free-air circulation, for 24 hours. At the end of this time it is again weighed and the loss of weight calculated to milligrams per square centimeter. Where large and delicate balances can not be had, the apparatus can be constructed on a smaller scale suitable for use with a balance of the ordinary size.

In the Sunlight.—The apparatus described above is enclosed in a wooden box having a circular opening the size of the soil-zinc cylinder. In the determination of the rate of evaporation, the apparatus, charged and weighed as above described, is exposed to the sun for a given period of time, say one hour. On the second weighing the loss represents the water evaporated. The time of year, time of day, velocity of wind and temperature, and degree of saturation of the air with aqueous vapor, should be noted. The data obtained can then be calculated to milligrams of water per square centimeter of surface for the unit of time.

Method b.—As in method *a* the determination may be made in the shade or in the sunlight. The rate of evaporation is, in this method, a diminishing one and depends largely on the reserve store of water in the sample at any given moment.

The same piece of apparatus may be used as in the determinations just described. After charging the sample with moisture all excess of water in the outer zinc vessel is removed and the rate of evaporation determined by exposure in an open room or in the sunlight, as is done in the operations already described.

Alternate Method.—The zinc cylinders used in determining saturation coefficient, may also be employed in determining the rate of evaporation. Each cylinder should be wrapped with heavy paper or placed in a thick cardboard receptacle, and all placed in a wooden box, the cover of which is provided with circular perforations, just admitting the tops of the cylinders, which should be flush with the upper surface of the cover.

Arranged in this way the cylinders previously weighed are exposed in the shade or to direct sunlight and reweighed after a stated interval. On account of the small surface here exposed in comparison with the total quantity of soil and moisture it is recommended to weigh the cylinders once only in 24 hours. The weighings may be continued for a fortnight or even a month.

In soils fully saturated with water the rate of evaporation is at first nearly the same on account of the surface being practically that of water alone. As the evaporation continues, however, the rate changes markedly with the character of the soil.

176. **Method of Wolff.**—In order to expose a larger surface to evaporation and to secure the results in a shorter period of time, Wolff fills cubes of 6 cm. sides made of wire-gauze, with fine earth, and weighs and suspends them in the laboratory near a window and near the balance.[25] The wire-gauze bottoms and sides are previously covered with filter paper to prevent loss of soil. The soil in the cubes may also be completely saturated with water and the rate of evaporation determined as just described.

177. **Estimation of Water Given up in a Water-Free Atmosphere.**—The air-dried sample, in quantities of from 5 to 10 grams in a thin layer on glass, is placed over a vessel containing strong sulfuric acid. It is then placed on a ground glass plate and covered with a bell jar. The sample is weighed at intervals of five days until the weight is practically constant.

This method is valuable in giving the actual hygroscopic power of a soil depending on its structure alone.

178. **Estimation of the Porosity of the Soil for the Passage of Gases.**—Some further notion of the physical state of the soil known as porosity, may also be derived by a study of the rate at which it will admit of the transmission of gases, as shown in 160. Another method for estimating this has been devised by Ammon.[26]

Air is compressed in two gas holders by means of a column of water of proper height to give the pressure required.

The tubes through which the air passes out of the gas holders are each furnished with a stop-cock and united with a glass tube having a side tube set in at right angles for carrying off the air.

The use of two holders makes it possible to carry on the experiment as long as may be desired, one holder being filled with air while the other is emptying. The common conducting tube is joined with a meter which is capable of measuring, to 0.01, the

[25] Landwirtschaftliche Jahrbücher, 2 : 381-3.

[26] Forschungen auf dem Gebiete der Agricultur-Physik, 1880, 211, 218.

volume of air passing through it. The pressure is regulated by means of the stop-cocks. The air passing from the meter is received in a drying tube filled with calcium chlorid. From the drying tube the air enters a drying flask filled below with concentrated sulfuric acid and above with pumice stone saturated therewith. Next the dried air passes through a worm, eight meters long, surrounded with water at a given temperature. The dried air thus brought to the desired temperature next enters the experimental tube. This tube is made of sheet zinc 125 centimeters in length and five centimeters in internal diameter. It is placed in an upright position, and about six centimeters from its upper end carries a small tube at right angles to the main one for connection with a water-filled manometer.

The upper and lower ends of the tube are closed with perforated rubber stoppers carrying tubes for the entrance and exit of the air.

In the inside of the zinc tube are found two close-fitting but movable disks, of the finest brass wire gauze, between which the material to be experimented upon is held.

The layer of fine soil is held between these disks and may be of such a depth as is required for the proper progress of the experiment. With soils of firm texture opposing a great resistance to the passage of the air the column of earth tested should be shorter than with light and very permeable soils. The experimental tube is surrounded with a water jacket, which may also be made of sheet zinc, carrying small tubes directed upwards for holding thermometers. The water jacket should be kept at the same temperature as the air which is used in the experiment.

The process of filling the tube, the amount of pressure to be used and the air and soil temperature, will naturally vary in different determinations.

The volume of air at a given pressure and temperature which passes a column of soil of a given length in a unit of time will give the coefficient of permeability.

179. **Determination of Permeability in the Open Field.**—A method for determining the rate of transmission of a gas through the soil in the field has been devised by Heinrich.[27]

[27] Beurteilung der Ackerkrume, 222.

A box C (Fig. 26) is made of strong sheet iron and has an opening below, 10 centimeters square, and a height of about 20 centimeters. At exactly 10 centimeters from the bottom, the box has a rim at right angles to its length so that it can be placed only 10 centimeters deep in the soil. The box holds a volume of earth equal to 1,000 cubic centimeters.

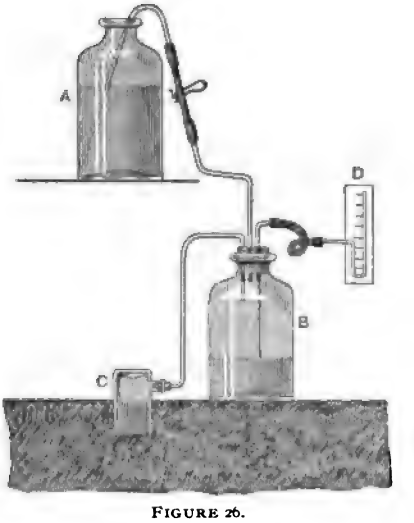


FIGURE 26.
METHOD OF HEINRICH.

The part of the box above ground is connected with the bottle B by a glass tube as indicated in the figure. The bottle B should have a capacity of about 10 liters. The air in B is forced out through C by water running in from the supply A and the pressure in B is recorded by the manometer D. The experiment should be tried on a soil thoroughly moist.

In measuring the pressure in B the water pressure should be cut off by the pinch-cock between A and B, and the pressure on the manometer observed after the lapse of one to two minutes.

MOVEMENT OF WATER THROUGH SOILS: LYSIMETRY

180. Porosity in Relation to Water Movement.—The intimate relation which water movement in a soil bears to fertility makes highly important the analytical study of this feature of porosity.

A soil deficient in plant food, in so far as chemical analysis is concerned, will produce far better crops when the flow of moisture is favorable than a highly fertile soil in which the water may be in deficiency or excess.

Aside from the actual rain-fall the texture of the soil, in other words its porosity, is the most important factor in determining the proper supply of moisture to the rootlets of plants. Even where the rain-fall is little, a properly porous soil in contact with a moist subsoil will furnish the moisture necessary to plant growth. This fact is well illustrated by the beet fields in Chino Valley, California. In this locality crops of sugar beets are produced without irrigation and almost without rain.

181. Methods of Water Movement.—The translocation of soil water is occasioned in at least two ways; namely,

1. By changing the porosity of a given stratum of soil.

2. By changing the amount of water a given stratum contains.

The following experiment by King illustrates a convenient method of studying this movement of water.[28]

On fallow ground of light clay soil, underlaid at a depth of eighteen inches by a medium-grained sand, water, to the amount of two pounds per square foot on an area of eight by eight feet, was slowly added with a sprinkler, samples of soil having been previously secured in six-inch sections down to a depth of three feet. The samples were taken along a diagonal of the square under experiment and one foot apart, the middle sample of the line being from the center of the area. The sampling and wetting occurred between one and three P. M., on July 22d, and on the evening of the 23d a corresponding series of samples was taken along a line parallel to the first but eight inches distant. The changes in the percentages of water in the soil are given in the following table, showing the translocation of water in soil due to wetting the surface:

	Per cent. of Water.		Difference	
Inches.	Before wetting.	After wetting.	In per cent.	In pounds per cu.
0– 6	14.00	22.23	+ 8.23	+ 2.873
6–12	15.14	15.71	+ 0.57	+ 0.199
12–18	16.23	15.75	— 0.48	— 0.213
18–24	17.70	16.92	— 0.78	— 0.347
24–30	16.76	14.41	— 2.35	— 1.032
30–36	15.51	15.21	— 0.30	— 0.132

[28] Wisconsin Experiment Station Seventh Annual Report, 134.

The figures given in the last column of the table are computed from the absolute dry weights of the upper three feet of soil as determined in a locality some rods from the place of experiment, and are therefore only approximations, but the error due to this cause is certainly small. It will be seen that while only two pounds of water to the square foot were added to the surface, the upper six inches contained 2.87 pounds per square foot more than before the water was added, and the second six inches contained 0.199 pounds more, and this too in the face of the fact that the evaporation per square foot from a tray sitting on a pair of scales close by, was 0.428 pound during the interval under consideration. Similar experiments were made by getting the samples of soil at 5.30 P. M. in one-foot sections down to four feet, at four equally distant places along the diagonal of a square six by six feet, and having the ground sprinkled. At the same time four similar sets of samples were secured on lines vertical to each of the sides of the square but four feet distant from them. The amount of water the soil contained was then determined, and at 11.30 A. M., 19 hours later, another series of samples was removed at points about four inches distant from the last and the amount of water determined with the result given below.

TRANSLATION OF WATER OCCASIONED BY WETTING THE SURFACE.

Depth of samples.	WET AREA.				AREA NOT WET.			
	Before wetting.		After wetting.		First samples.		Second samples.	
	Per cent. of water.	Pounds of water per cubic foot.	Per cent. of water.	Pounds of water per cubic foot.	Per cent. of water.	Pounds of water per cubic foot.	Per cent. of water.	Pounds of water per cubic foot.
0–12 inches	16.86	11.78	20.15	14.06	17.72	12.38	18.27	12.75
12–24 "	17.76	15.79	19.71	17.52	19.18	17.05	19.94	17.72
24–36 "	16.76	14 73	17.72	15.58	16.97	14.92	17.52	15.40
36–48 "	15.01	14.03	16.47	15.40	15.49	14.48	15.16	14.17
Averages	16.59	14.08	18.51	15.64	17.34	14.71	17.71	15.01
Total am't of water	.....	56.33	.....	62.56	.....	58.83	.....	60.04
Amount of change.	.....	.....	.....	6.23	.....	.....	.....	1.21

The above data show sufficiently well the method of investigation to be pursued in studies of this kind.

182. Capillary Movement of Water.—The method of investigation proposed by King consists in getting samples of soil at intervals of one, two, three, or four feet in depth, and determining the amount of moisture in each in connection with the amount of rain-fall during the period.[29] The quantity of water contained in a given soil, at various depths and on different dates, is shown in the following table:

Depth in feet.	Date	Per cent. water	Pounds per cubic foot.	Increase or decrease. Pounds per cubic foot.
1	March 8th	24.33	16.98	.....
1	April 18th	22.37	15.61	—1.37
2	March 8th	15.80	14.05	.....
2	April 18th	21.64	19.24	5.19
3	March 8th	11.16	9.81	.....
3	April 18th	16.24	14.27	4.46
4	March 8th	7.87	7.36	.....
4	April 18th	11.19	10.46	3.10

The rain-fall during the interval was 4.18 inches, equal to 21.77 pounds per square foot.

183. Lateral Capillary Flow.—To determine the lateral capillary flow of water in a soil the following method, used by King, may be employed:[30]

A zinc lined tray, six by six feet in area and eight inches deep, is filled with a soil well packed. In one corner of this tray a section of five inches of unglazed drainage tile, having its lower end broken and jagged, is set and the dirt well filled in round it. By means of a Mariotte bottle water is constantly maintained in the bottom of this tile, three-quarters of an inch deep, so that it will flow laterally by capilliary action into the adjacent soil, the object being to determine the extent and rate of capillary flow laterally.

The water content of the soil is determined at the time of starting the experiment, on the circumferences of circles described with the tile as a center, the distance between the circles being one foot. At stated periods, usually at intervals of one day, the content of moisture is again determined at the same points. The investigations show that the lateral movement of water in the soil is not rapid enough to extend much beyond three feet in 31

[29] Wisconsin Experiment Station Seventh Annual Report, 139.

[30] Wisconsin Experiment Station Seventh Annual Report, 145.

days, for beyond that distance the soil was found to be drier than at the beginning of the experiment. A record is to be kept of the amount of water delivered to the soil by weighing the supply bottle at intervals, and the rates given at which the soil takes up the water in grams per hour and pounds per day. Also the amount of flow per square foot of soil section together with the mean daily evaporation should be noted. The mean flow per foot of soil section is computed on the assumption that the outer face of the zone of completely saturated soil is the delivering surface. In King's work this point, as nearly as could be determined, was 12 inches from the corner of the tray and hence the figures at best can only be regarded as approximations. The method of stating results is shown in the following table:

SHOWING THE RATE OF LATERAL CAPILLARY FLOW OF WATER IN CLAY LOAM.

Date.	No. of days.	Total mean, hourly flow, grams.	Total mean, daily flow, pounds.	Mean daily flow per square foot, pounds.	Mean daily, evaporation, pounds.
Jan. 28 to Feb. 2....	5	70.70	3.73	2.38	.....
Feb. 2–7.....	5	85.98	4.54	2.91	.....
Feb. 7–12.....	5	79.33	4.19	2.64	.....
Feb. 12–17....	5	79.41	4,19	2.64	0.598
Feb. 17–22.....	5	70.79	3.74	2.38	0.534
Feb. 22–28.....	6	59.89	3.16	2.01	0.451
Feb. 28 to March 6..	6	60.74	3.21	2.04	0.458
Mar. 6–13	7	60.37	3.14	2.00	0.448
Means.....				2.38	0.498

From this table it will be seen that the flow of water in the soil varied in rate, being slower during the first five days than in the succeeding 15 days. After 20 days the flow dropped again to the beginning rate and then fell below, but remained quite constant during the following 19 days. For the sake of uniformity in units of measure the daily quantity of flow should be given in kilograms when the hourly flow is given in grams.

184. Causes of Water Movement in the Soils.—The movement of water is due to two forces, *viz.*, gravitation and capillarity.

The mechanical and mathematical principles governing the movement of water in soils are discussed by Briggs.[81] When the

[81] Bulletin No. 10, Division of Soils, Dept. of Agriculture.

flow of water due to gravitation ceases a condition of equilibrium is established between the force of gravitation and the forces opposing it. According to Briggs there is no sharply-drawn line between these two quantities of water. The relative proportion depends, among other factors, upon the texture and structure of the soil, the surface tension of the soil water, the temperature, and the length of the column of soil considered. The importance of this last factor can be shown from the following considerations: Suppose we have 100 cubic inches of soil packed into 100 cubical boxes without bottom or top, each containing 1 cubic inch. Suppose the soil in each box to be saturated with water. There will be a free water surface at the top and at the bottom of each box. By means of forces existing in these surfaces the water in each cube is enabled to overcome the attraction of gravity, so that each cube is able to retain an amount of water equal to that necessary to produce saturation. In this case, therefore, there is no gravitation water. Suppose now that these cubical boxes are built up in a vertical column 100 inches high. The water surfaces previously existing at the top and bottom, respectively, of two cubes now disappear when one cube is placed on top of the other. Instead of having 200 surfaces as before, we now have only two surfaces, and they are called upon to support a column of water 100 times as high as before. This they are unable to do, and water begins to drip from the lower surface. This water, which was previously what we have termed capillary, now becomes gravitational in its nature, due simply to a change in the length of the column. If the water in the soil was held in vertical capillary tubes running throughout the length of the column the water in each tube would simply fall until the two surfaces were able to support the weight of the liquid. In the soil, however, we have a different condition. As the water begins to leave the upper part of the column new surfaces are developed *within* the soil. As the water continues to drain away, these surfaces become more efficient in a way which is easily explained, and finally there comes a time when the opposing force exerted by these surfaces is sufficient to balance the weight of the liquid and the drainage ceases.

185. Effects of Salts on Water Movement.—Since the effectiveness of capillarity in opposing gravitation is dependent largely on the surface tension of the aqueous soil solution the addition of fertilizers, by changing this tension, may influence in a marked degree the translation of water in the soil. According to Briggs any change in the surface tension of the soil moisture tends to bring about an adjustment of the water throughout the whole mass of soil. If the surface tension of the water in the upper layers of a soil is increased, water is drawn toward that point. Since the surface tension of most salt solutions is higher than that of water and the surface tension increases with the concentration of the solution, it might be expected that any salt used as fertilizer a solution of which has a high surface tension would increase the amount of water in the soil.

It must be remembered, however, that the surface tension of solutions is very greatly decreased by the addition of very small quantities of certain organic substances produced through the decomposition of vegetable matter. This action is especially marked where there are present substances of an oily nature which do not go into solution, but spread out over the surface in an extremely thin film. Owing to such substances being continually produced by the decay of organic matter, the surface tension of the soil moisture is kept very low and could be only slightly influenced by the addition of salts. The application of substances to the soil for the purpose of changing its water content through a change in the surface tension, would not therefore necessarily be productive of marked results, except as indicated below.

186. Effect of Salt Solutions on Soil Moisture.—The mineral fertilizers, as a rule, as has already been stated, increase the surface tension of water, while organic matters in solution decrease it. But it must not be forgotten in this connection that but little of the organic matter in the fertilizers employed for the experiment passes into solution. In general, the results of experiment are in harmony with the well known effect of magnesium, sodium, and potassium chlorids, and sodium nitrate, to make the soil more moist in dry weather, and the opposite effect is produced by the application of soluble organic matter.

187. **Method of Preparing Soil Extracts.**—The soil extracts used in determining surface tension may be prepared in different ways. A common method of procedure is as follows:

Ten grams of the soil are rubbed up with from 15 to 20 cubic centimeters of distilled water and allowed to stand for 24 hours with frequent stirring. Any fine particles not removable by a paper filter are neglected, although they may give a turbid appearance to the solution. The solution may be secured perfectly clear by filtering through porcelain.

188. **Lysimetry.**—The process of measuring the capacity of a soil to permit the passage of water and of collecting and determining the amount of flow and determining soluble matters therein is known as lysimetry. In general, the rate at which water will pass through a soil depends on the fineness and approximation of its particles. Water will pass through coarse sand almost as rapidly as through a tube, while a fine clay may be almost impervious to its transit. The study of the phenomena of filtration through soil, and the methods of quantitatively estimating them, are therefore closely related to porosity.

Two cases are to be considered, *viz.:* First, percolation through samples of soil prepared for the special purpose, and second, the passage of the water through soil *in situ,* whether it be virgin or cultivated.

The determination of the rate of flow through a soil in laboratory samples, gives valuable information is respect of its physical properties, while the same determination made on the soil *in situ,* has practical relations to the supply of moisture to growing plants, and the waste of valuable plant food in the drainage waters. The determination of the rate of flow of water through a small sample, disturbed as little as possible in its natural condition, is classed with the first divisions of the work, inasmuch as the removal of a sample of soil from a field, and its transfer to the laboratory, subjects it to artificial conditions, even if its texture be but little disturbed by the removal.

189. **Measurement of Rate of Percolation in a Soil Sample.**—In order to measure approximately the power of the soil for permitting the passage of water, a box, about 25 centimeters

high and having a cross section of about three centimeteers square, has been recommended. Below, this box has a funnel-shaped end with a narrow outlet tube, which at its lower end is closed with cotton, in such a way that a portion of the cotton extends through the stem of the funnel. A little coarse quartz sand is scattered over the cotton and afterwards the funnel part of the appartus filled with it. The sand and cotton are saturated with water and the apparatus weighed. The box is then filled with the fine sample of earth, with light tapping, until the depth of earth has reached about 16 centimeters. The apparatus, after the addition of the air-dried earth, is again weighed to determine the amount of earth added, and the soil is then saturated by the careful addition of water. After the excess of water has run down the funnel, the total quantity of absorbed water is determined by reweighing the apparatus and the total water-holding power of the soil is determined. There is carefully added, without stirring up the surface of the soil, a column of water eight centimeters high, making in all from 60 to 70 grams. The time is observed until the water ceases to drip from the funnel. The dripping begins immediately after the water is poured on and ceases as soon as the liquid on the surface of the soil has completely disappeared. On the repetition of this operation a longer time for the passage of the water is almost always required than at the first time. The experiment, therefore, must be tried three or four times and the mean taken.

190. **Method of Welitschowsky.**—The soil is placed in the vessel *a*, Fig. 27, which is cylindrical in shape and five centimeters in diameter.[32] The lower end of the cylinder is closed with a fine wire-gauze disk and the upper end is provided with an enlargement for the reception of the tube *b*, which is connected to *a* with a wide rubber band. The lower end of the tube *b* is also closed with a wire-gauze disk. These tubes may be conveniently made of sheet zinc. The tube *b* carries on the side, at distances of 10 centimeters, small tubes of 15 millimeters diameter. On the opposite side it is provided with a glass tube set into a side tube near the bottom for the purpose of showing the height of the water.

[32] Forschungen auf dem Gebiete der Agrikultur-Physik, **10** : 202.

The side tube carrying the water gauge is provided with a stop-cock as shown in the figure.

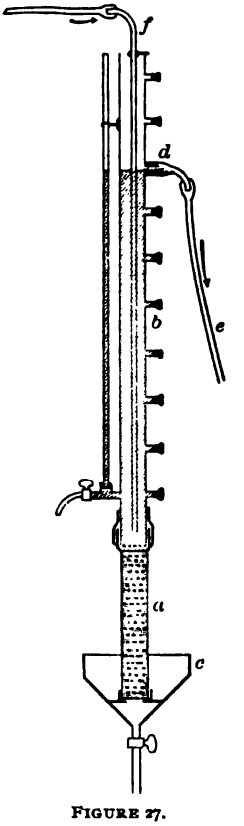


FIGURE 27.
METHOD OF
WELITSCHOWSKY.

In conducting the experiment, after the apparatus has been arranged as described, the small lateral tubes are, with one exception, closed with stoppers. On the open one, *d*, a rubber tube is fixed for the purpose of removing the water. The required water pressure is secured by taking the lateral opening corresponding to the pressure required. Water is introduced into the apparatus slowly through the glass tube *f*.

The water rises to *d* and then any excess flows off through *e*.

By a proper regulation of the water supply the pressure is kept constant at *d*. The water flowing off through *a* is collected by the funnel and delivered to graduated flasks where its quantity can be measured for any given unit of time. Since the rate of flow at first shows variations, the measurement should not be commenced until after the flow becomes constant.

In general, the experiments should last 10 hours, and, beginning with a water pressure of 100 centimeters, be repeated successively with pressures of 80, 60, 40 and 20 centimeters, etc., In coarse soils, or with sand, one hour is long enough for the experiment.

191. **Statement of Results.**—In the following tables the results for 90 centimeters, 70 centimeters, etc., are calculated from the analytical data obtained for 100 centimeters, 80 centimeters, etc.

Similar sets of data have been collected with powdered limestone, clay and humus.

The general conclusions from the experiments are as follows:

MATERIAL—QUARTZ SAND.

No. of Exp.	Diameter of sand particles in mm.	Water pressure in cm.	Liters of Water Passing in Ten Hours. Thickness of Soil Layer. 10 cm.	20 cm.	30 cm.
1.	0.01—0.71	10	0.214	0.187	0.151
		20	0.282	0.198	0.154
		30	0.320	0.209	0.158
		40	0.358	0.220	0.161
		50	0.396	0.231	0 165
		60	0.434	0.242	0.168
		70	0.472	0.253	0.172
		80	0.510	0.264	0.175
		90	0.548	0.275	0.179
		100	0.586	0.286	0.182
2.	0.071—0.114	10	2.194	1.724	1.425
		20	2 898	2.012	1.578
		30	3.602	2.300	1.731
		40	4.306	2.588	1.884
		50	5.010	2.876	2.037
		60	5.714	3.164	2.190
		70	6.418	3.452	2.343
		80	7.122	3.740	2.496
		90	7.826	4.028	2.649
		100	8.530	4.316	2.802

1. Clay (kaolin) and humus (peat) are almost impermeable to water, and fine quartz and limestone dust are also very impermeable.

2. The permeability of a soil for water increases as the particles of the soil increase in size, and when particles of different sizes are mixed together the permeability approaches that of the finer particles.

3. The quantity of water passing through a given thickness of soil increases with the water pressure but is not proportional thereto, increasing less rapidly than the pressure.

4. The quantity of water passing under a given pressure is inversely proportional to the thickness of the soil layer when the particles are very fine and the pressure high.

192. Method of Whitney.—To determine the permeability of the soil or subsoil to water or air, as nearly as possible, in its natural condition in the field, Whitney uses the following method:—

A hole should be dug, and the soil and subsoil on one side removed to the depth at which the observation is to be made. A column of the soil or subsoil, two inches or more square, and four or five inches deep, is then to be carved out with a broad bladed knife, or a small saw can be conveniently used for cutting this out. A glass or metal frame, a little larger than the sample and three or four inches deep, is slipped over the column of soil, and melted paraffin is run in slowly to fill up the space between the soil and the frame. The soil is then struck off even with the top and bottom of the frame, preferably with a saw, or at any rate taking care not to smooth it over with a knife, which would disturb the surface and affect the rate of flow. The frame is then placed upon some coarse sand or gravel, contained in a funnel, to prevent the soil from falling out and to provide good drainage for the water to pass through. Another similar frame can then be placed on top and secured by a wide rubber band. A little coarse sand, which has been thoroughly washed and dried, is then placed on the soil, and water carefully poured on until it is level with the top of the frame. When the water begins to drop from the funnel more water must be added to the top, so as to have the initial depth of water over the soil the same in all the experiments. A graduated glass is then pushed under the funnel, and the time noted which is required for a quantity of water to pass through the soil. The quantity usually measured is equivalent to one inch

in depth over the soil surface. In getting the sample, root and worm-holes are to be avoided, and these are particularly troublesome in clay lands.

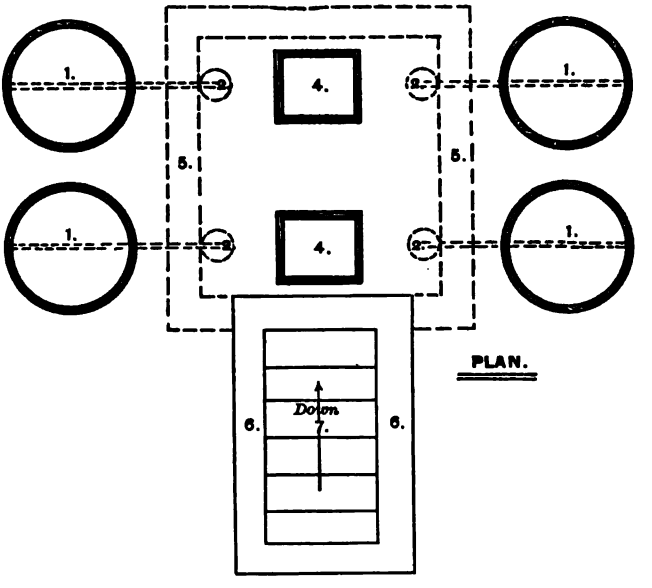
193. **Measurement of Percolation Through the Soil in Situ.**—If lateral translocation could be prevented, the measurement of the quantity of water descending in the soil through a given area would be a matter of simplicity. But to secure accurate results all lateral communication of a given body of soil with adjacent portions must be cut off. Various devices have been adopted to secure this result. An elaborate system of lysimetric measurements is illustrated by the data secured with the apparatus erected by the Agricultural Experiment Station, of Indiana.

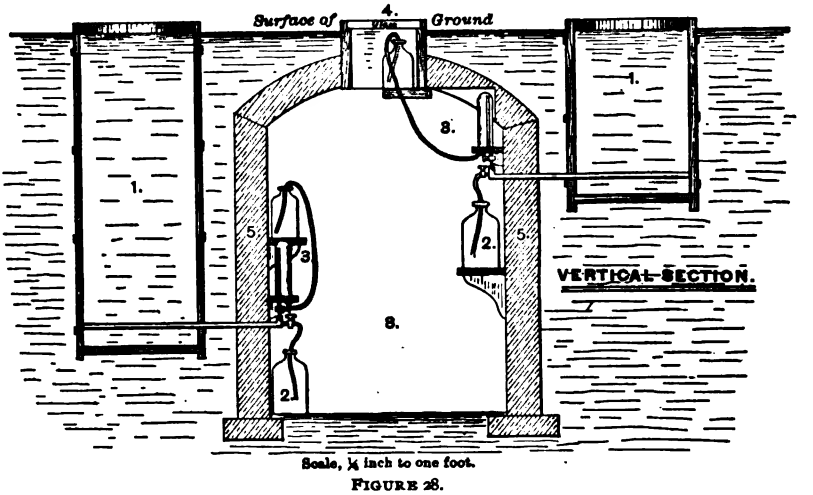
The plan and section of the apparatus are shown in Fig. 28.

Each lysimeter box, when finished, resembles somewhat a hogshead with one head. The sides, however, are perfectly straight inside, having a slight thickening in the center, for making them stronger. The sides and bottom of the apparatus are constructed of oak and lined with sheet copper carefully soldered so as to be water-tight. Six inches above, and parallel to the bottom of each of the boxes, is a perforated copper tube, which extends entirely across the lysimeter, and passing through one of the sides connects the box with an underground vault in which the observations are made. These tubes give an outlet to the drainage water, as described further on. The lysimeters are made of any required depth, the two which are shown in section being three and two-thirds and six and two-thirds feet deep, respectively.

The following method is employed for filling them with soil: There is first placed in the bottom of each tank a layer six inches deep of fine sand, sifted and washed, which fills them up to the level of the drainage tubes. The lysimeters are then filled with fine, sifted surface soil, to the depth of three and six feet, respectively, and leaving two inches of the boxes projecting above the surface of the soil so that each one will receive exactly its proper share of the rain-fall.

The tanks of the other pair, which are the same size as the first, are filled in a different way. The containers are placed over vertical columns of soil *in situ*, which are obtained by digging away all





Scale, ¼ inch to one foot.

FIGURE 28.

GROUND PLAN AND VERTICAL SECTION OF LYSIMETERS AND VAULTS SHOWING POSITION OF THE APPARATUS.

1, 1, 1, 1, Lysimeters.
2, 2, 2, 2, Receiving bottles.
3, 3, Supplying apparatus.
4, 4, Skylights.
5, 5, 5, 5, Wall of vault.
6, 6, Brick walls.
7, Entrance steps.
8, Vault.

the surrounding soil and leaving the columns standing. The shorter tank is sunk in this way to within two inches of its entire length. It is then tipped over carrying the column of soil with it. Six inches of the subsoil are then removed, when the drainage tube and sand are put in, as in the first pair, and the bottom of the tube soldered in place. The longer box is in the same way filled, as far as possible, with the soil in place, but a gravelly nature of the soil may render it impossible to do the filling with a single column unbroken, and in this case the gravel and sand from the lower portion of the soil may be filled in separately. The drainage tube and bottom of sand are placed in the longer tank in the same way as in the shorter.

The purpose of placing sand at the bottom of each container is to offer a porous stratum in which free water may collect and rise to the level of the perforated copper tube, which would prevent any further rise by conveying the surplus above into the vault as drainage water. The soil above the tube will therefore be constantly drained and the sand below constantly saturated, unless the water be drawn up by the capillary action of the soil as the result of evaporation from the surface.

By means of a proper arrangement within the vault, of a kind of mariotte bottle, the water may be caused to flow back through the drainage tube into the tank to take the place of that lost by evaporation, and thus maintain the level of free water just below the drainage tube. The water flowing back to the tank and the amount of drainage water, are carefully measured by a system of graduated tubes.

The lysimeters thus constructed represent tile- drained land; in one case the tile being three feet below the surface and in the other six feet below. The drainage waters collected in the receiving bottles can be measured and analyzed from time to time, as occasion may require, to determine the amount of plant food which is removed.

194. **Improved Method of Deherain.**—Deherain's earlier experiments were made in pots containing about 60 kilos of soil.[28] These vases serve very well for some kinds of plants, but there are other kinds which do not grow at all normally when their

[28] Annales Agronomiques, **16** : 337; **17** : 49; **18** : 237; **19** : 69.

FIGURE 29.
DEHERAIN'S APPARATUS FOR COLLECTING DRAINAGE WATER.

roots are imprisoned. For instance, in pots, even of the largest size, wheat is always poor, beets irregular, maize never acquires its full development, and the conclusions which can be drawn from the experiments can not be predicated of the action of the plant under conditions entirely normal.

It is necessary therefore to carry on the work in an entirely different way, and to construct boxes so large as to make the conditions of growth entirely normal. The arrangement of these boxes is shown in Fig. 29.

They are placed in a large trench, two meters wide, one meter deep, and 40 meters long. There are 20 boxes in this trench, the upper surface of each having an area of four square meters. The boxes are one meter deep, and therefore can contain four cubic meters of soil. The sides and bottoms of the boxes are made of iron lattice work, covered with a cement which renders them impervious to water.

The bottom inclines from the sides towards the middle, and from the back to the front, thus forming a gutter which permits of the easy collection of the drainage. The drainage water is conveyed, by means of a pipe and a funnel, into a demijohn placed in the ditch in front of the apparatus, as shown in the figure. These receptacles stand in niches under the front of the cases, and are separated by the brick foundations. Access to them is gained by means of the inclined plane shown in the figure, and this plane permits the demijohns in which the drainage water is collected, to be removed with a wheelbarrow for the purpose of weighing. This apparatus is especially suitable for a study of the distribution of the nitrogen to the crop, the soil and the drainage waters. The loss in drainage waters of phosphoric acid is insignificant in comparison with the loss in nitrogen and potash.

The boxes having been placed in position they are filled with the natural soil, to the depth of one meter, in such a way that the relative positions of the soil and subsoil are not changed.

While the soil is transferring to the boxes it is carefully sampled in order to have a portion representing accurately the composition of both the soil and subsoil. These samples are subjected to analysis and the quantities of nitrogen, phosphoric acid, and potash contained therein carefully noted.

One or two boxes should be left without crop or fertilizer to determine the relations of the soil and subsoil to the rain-fall, and three or four should be kept free of vegetation and receive treatment with different fertilizers in order to determine the influences of these on the deportment of the soil to rain-fall. The rest should be seeded with plants representing the predominant field cultures of the locality, and some of them should be fertilized with the usual manures used in farm culture.

195. IMPORTANCE OF ANALYSIS OF DRAINAGE WATERS.

Since certain mineral principles have been recognized as necessary to vegetation, much study has been given to the conditions of their assimilation. At first it was assumed that they cannot be absorbed except they become dissolved in the water of the soil. The memorable experiments of Huxtable and Thompson and of Way upon the absorbent properties of earths have modified this opinion, and several eminent savants, Liebig among others, have attributed to the roots the power to assimilate directly the alkalies and the phosphates precipitated upon the particles of arable soil. Quite a large number of experiments have been instituted upon this subject, especially in Germany, but there are few records of analyses of the solutions which are really found in the cultivated soils, analyses which seem however essential to the question under discussion. Schloesing is of the opinion that drainage waters, collected after having been filtered through a meter of earth, whose poverty has served for illustration, cannot faithfully represent the solution which the arable layer imbibes.[84] The lysimeters of Fraas and Zoeller, which give the drainage water from this layer, furnish some elements of discussion which are more useful but the soils give up their water only under certain conditions independent of the observer, and the lysimeters cannot possibly collect the solution existing at a given moment, at a given depth, under given conditions of temperature, and of condition of the atmosphere and of moisture. The method proposed by Schloesing to avoid these difficulties is described in part eighth.

[84] Comptes rendus, **70** : 94.

PART FOURTH

MECHANICAL ANALYSIS OF SOILS

196. Purpose of Mechanical Analysis.—By an optical mineral analysis of soils the investigator determines the character of the particles that can be seen with the eye or with the aid of the microscope. By a chemical analysis he determines the materials entering into the constitution of these particles. The object of mechanical analysis is to determine the size of the various mineral particles making up the bulk of the soil and to separate these particles into groups of approximately the same size. Such a separation throws light on the relation of the soil to moisture and permeability to the rootlets of plants, but gives no indication whatever of the quantity of plant food which the soil may contain.

197. General Principles.—The underlying principle in the mechanical analysis of soils is based on sifting or on sedimentation or, in other words, the rate at which segregated particles of soil will fall through a liquid medium, usually water. The larger particles and even the fine sand will rapidly sink while the smaller particles and the fine clays may remain in suspension for hours and days. Since the larger particles sink to the bottom too rapidly to admit of separation by sedimentation they must be separated into groups of any given size by sifting. Since the finest silt may remain in suspension for days and even weeks, it is usually determined by evaporation or by difference after having weighed all the larger classes of particles. Since much of the material of the larger particles, especially of lime particles, may pass into solution in the water used as a solvent this method of determination of the suspended particles is not strictly accurate. It is important in all cases that any flocculated material, that is small aggregates formed by the adhesion of smaller particles, be broken up as perfectly as possible into their constituent elements.

It is evident that should an upward movement in the liquid be

instituted equal in velocity to the natural descent of any particle in obedience to the impulse of gravity, that particle would remain in *situ* and all other particles having a less velocity of descent would be carried upward. Hence, it follows that the separation of the soil into group particles may also be effected by means of an upward current of water moving at successively increasing velocities.

In respect of the liquid in which the separation is effected water has been uniformly employed. By reason of its solvent action on many of the soil components, especially those in which lime and potash are found, its use is attended with certain difficulties. No other liquid, however, has been proposed to which fewer objections could be made. The ideal liquid is one that would exercise no solvent action, favor the disaggregation of the flocculated soil particles and permit the freest movement of the single particles.

Precedent to the separation of the particles of which a soil is composed into groups of approximately a given size, the removal of those parts of the soil of excessive fineness even beyond the power of microscopic identification becomes a necessity. Such particles approach a state of subdivision and freedom from methodical arrangement which characterize that class of gelatinous non-crystalline matters known under the general name of colloids.

198. Suspended Colloids.—The clay which remains in suspension in water for 24 hours or longer may be regarded as a colloid body in suspension. Such a body, as has been shown by experiment, remains in suspension only in the absence of an electrolyte in the solution or when an electrolyte is present in a certain minimal quantity. The suspension of these fine particles in the light of this theory is ascribed to an electrical static charge which may be either positive or negative. Thus water which carries any notable quantity of a soluble salt which plays the rôle of an electrolyte will not be capable of holding a clay in suspension for any length of time. When an electrolyte such as common salt, alum or a mineral acid is added to water carrying suspended clay the static charges are discharged or so modified as to permit of the coagulation and consequent subsidence of the colloid body. This

theory of clay suspension is in harmony with many of the well known results of treating such suspended matter both with electrolytes and non-electrolytes.

According to Noyes there are two classes of colloidal mixtures.[35]

As types of these are cited aqueous solutions of gelatine and of colloidal arsenious sulphid. The one gelatinzes on cooling, the other does not.

The former is not coagulated by the addition of moderate amounts of salts, the latter is. The former class may be designated as colloidal solutions, the latter as colloidal suspensions, Strong electrolytes tend to cause coagulation in colloidal suspensions and the ion carrying the charge opposite to that borne by the suspended colloid is mainly responsible for the coagulation that takes place.[36]

199. **Effect of Adding Non-Electrolytes to Suspended Clay.**—The progress of flocculation may be retarded by the addition of certain substances such for instance as ammonia to clay water. To be in harmony with the above theory such bodies should act in some way either to increase the static charge of the suspended particles or to diminish the power of an electrolyte to neutralize them. The efficiency of ammonia for this purpose has been studied by Briggs,[37] who has shown that ammonia has a very marked effect in breaking up the flocculations of the clay particles, and in increasing the quantity of the group approximately .005 millimeter, and below in diameter. This influence, however, is not apparent in strongly alkaline soils.

199[a]. **Separation of Colloids from the Soil.**—In the method of separating sand and clay by centrifugal action in a liquid heavier than water Sjollema has developed a method of separating the colloidal bodies in a state of approximate purity.[38]

For the method of separation reference is made to a paragraph further along. (Paragraph 268).

[35] Journal American Chemical Society, 27 : 86.

[36] Noyes—Presidential Address—Journal American Chemical Society, 27 : 85, et seq.

[37] Bulletin 24, Bureau of Soils, 22.

[38] Die landwirtschaftlichen Versuchs-Stationen, 1905 : 58, 70

For the microscopic examination of the separated colloid staining with an aqueous solution of methyl violet is recommended. Only the colloidal particles of the mass take the stain.

The colloidal matter prepared as described further along is subjected to analysis to determine its value for plant nourishment.

THE FLOCCULATION OF SOIL PARTICLES.

200. Relation of Flocculation to Mechanical Analysis.—The tendency of the fine particles of silt to form aggregates, which act as distinct particles of matter, is the chief difficulty connected with the separation of the soil into portions of equal hydraulic value by the silt method of analysis. This tendency has been discussed fully by Johnson[39] and Hilgard.[40]

201. Illustration of Flocculation.—A sediment, consisting of particles of a water velocity equal to one millimeter per second, is introduced into an ordinary conical elutriating tube placed vertically, in which the current of water entering below performs all the stirring which the particles receive.

A current of water corresponding to a velocity below one millimeter per second will, of course, not carry any of the particles out at the top of the cylindrical tube, but will keep them moving through the conical portion of the tube. If now the current be increased until its velocity is greater than one millimeter per second after having run at the slower velocity for fifteen or twenty minutes, very little of the sediment will pass over, although theoretically the whole of it should. Even at a velocity of five millimeters per second, much of the sediment will remain in the tube. This, of course, is due to the coagulation of the particles into molecular aggregates having a higher hydraulic value even than five millimeters per second. These aggregates can be broken up by violent stirring or moderate boiling, and the sediment reduced again to its proper value. The conclusions which Hilgard derives from a study of the above phenomena are as follows:

1. The tendency to coagulation is, roughly, in an inverse ratio to the size of the particles. With quartz grains it practically

[39] Connecticut Agricultural Experiment Station, Annual Report, 1877.

[40] American Journal of Science, 1879 [3], 17 : 205.

ceases when their diameter exceeds about two-tenths of a millimeter having a hydraulic value of eight millimeters per second. The size of the aggregates formed follows practically the same law as above. Sediment of 0.25 millimeter hydraulic value will sometimes form large masses like snow-flakes on the sides of the elutriator tube.

2. The degree of agitation which will resolve the aggregates into single grains is inversely as the size of the particles; or, more properly perhaps, inversely as their hydraulic value.

3. The tendency to flocculation varies inversely as the temperature. So much so is this the case that Hilgard at one time contemplated the use of water at the boiling point in the mechanical analysis of soils, in place of mechanical stirring.

4. The presence of alcohol, ether, and of caustic or carbonated alkalies, diminishes the tendency to flocculation, while the presence of acids and neutral salts increases it.

5. As between sediments of equal hydraulic value, but different densities, the tendency to flocculation seems to be greater with the less dense particles.

In regard to the mechanical actions which take place between the particles, Hilgard considers them as irregular spheroids, each of which can at best come in contact at three points with any other particle. The cause of aggregation cannot therefore be mere surface adhesion independent of the liquid, and the particles being submerged there is no meniscus to create an adhesive tension.

Since experiment shows that the flocculative tendency is measurably increased by the cohesion coefficient of the liquid, it seems necessary to assume that capillary films of the latter interposed between the surfaces of solids create a considerable adhesive tension even in the absence of a meniscus.

202. Effect of Potential of Surface Particles.—Whitney suggests that this attraction is due to the potential of the surface particles of solids and liquids.[41] The potential of a single water particle is the work which would be required to pull it away from the surrounding water particles and remove it beyond their sphere of attraction.

[41] Bulletin 4, Weather Bureau, Department of Agriculture, 19.

For simplicity, it may be described as the total force of attraction between a single particle and all other particles which surround it. With this definition, it will be seen that the potential of a particle on an exposed surface of water is only one-half of the potential in the interior of the mass, as half of the particles which formerly surrounded and attracted it were removed when the other exposed surface of water was separated from it. A particle on an exposed surface of water, being under a low potential, will therefore tend to move toward the center of the mass where the potential, *i. e.*, the total attraction, is greater, and the surface will tend to contract so as to leave the fewest possible number of particles on the surface. This is surface tension.

If, instead of air, there is a solid substance in contact with the water, the potential will be greater than on an exposed surface of the liquid, for the much greater number of solid particles will have a greater attraction for the water particles than the air particles had. They may have so great an attraction that the water particle on this surface, separating the solid and liquid, may be under greater potential than prevails in the interior of the liquid mass. Then the surface will tend to expand as much as possible, for the particles in the interior of the mass of liquid will try to get out on the surface. This is the reverse of surface tension. It is surface pressure, which may exist on a surface separating a solid and liquid.

Muddy water may remain turbid for an indefinite time, but if a trace of lime or salt be added to the water the grains of clay flocculate, that is, they come together in loose, light flocks, like curdled milk, and settle quickly to the bottom, leaving the liquid above them clear. Ammonia and some other substances tend to prevent this and to keep the grains apart if flocculation have already taken place.

If two small grains of clay, suspended in water, come close together they may be attracted to each other or not, according to the potential of the water particles on the surface of the clay. If the potential of the surface of water is less than that of the particle in the interior of the mass of liquid, there will be surface tension, and the two grains will come together and be held with some

force, as their close contact will diminish the number of surface particles in the liquid. If, on the other hand, the potential of the particle on the surface of the liquid is greater than of the particle in the interior of the mass, the water surface around the grains will tend to enlarge, as there will be greater attraction for the water particles there than in the interior of the mass of liquid, and the grains of clay will not come close together and will even be held apart, as their close contact would diminish the number of surface particles in the liquid around them.

203. Influence of Surface Tension.—Hilgard supposes that the surface tension which is assumed to exist between two liquid surfaces must exert a corresponding influence between the surfaces of solids and liquids, apart from any meniscal action.

It is then to be expected that the adhesion of the particles constituting one of these floccules will be very materially increased whenever the formation of menisci between them becomes possible by the removal of the general liquid mass. Suppose one of the floccules to be stranded, it will, in the first place, remain immersed in a sensibly spherical drop of liquid. As this liquid evaporates, the spherical surface will become pitted with menisci forming between the single projecting particles, and as these menisci diminish their radius by still further evaporation, the force with which they hold the particles together will increase until it reaches a maximum. As the evaporation progresses beyond this point of maximum, the adhesion of the constituent particles must diminish by reason of the disappearance of the smaller menisci, and when finally the point is reached when liquid water ceases to exist between the surfaces, the slightest touch, or sometimes even the weight of the particles themselves, will cause a complete dissolution of the floccule, which then flattens down into a pile of single granules.

In regard to natural deposits from water, Hilgard supposes that they are always precipitated in a flocculated state. The particles of less than two-tenths millimeter diameter are carried down with those of a larger diameter having much higher hydraulic value. Thus the deposition of a pure clay can take place under only very exceptionable circumstances.

Whitney, on the other hand, suggests that grains of sand and clay carry down mechanically the particles of fine silt and clay as they settle in a turbid liquid in a beaker; and it is often difficult to wash out a trace of fine material from a large amount of coarse particles, for this reason, although there may be no trace whatever of flocculation.

204. Quincke's Theory.—Quincke presents an ingenious theory in regard to the flocculation of turbid solutions.[42] His theory is that on the surface of the flocks, at least for a short time after their formation, oily, viscous fluid exists. In the case of kaolin, and probably other suspended silts from soils, this viscous fluid is supposed to be colloidal silicic acid. On the surface of separation of this oily fluid with the surrounding aqueous fluid, a surface tension acts and air bubbles are separated as in the limit of two heterogeneous fluids. Probably changes of the surface tension of the boundary of oily and aqueous fluid, and the periodical spreading of heterogeneous liquid, will excite vortices and join together the small suspended particles to form the flocks. In the case of kaolin turbidity, Quincke observed, after two months, a great many flocks adhering to the shadow side of the glass. Under the microscope the flocks showed threads or tubes of a downward flown liquid, with spheroidal enlargements or contractions. A sediment on the bottom of the glass cylinder had the appearance of solidified liquid, containing deformed bubbles and coherent foam cells, smooth spheres of .002 to .0004 millimeter in diameter, having greater refractive power than the neighboring particles. In this case, the particles of kaolin, as above assumed, have been covered by the influence of the water with an oily, viscous fluid, probably silica hydrate, on the surface of which another fluid has been spread out. The periodical spreading had combined the suspended kaolin particles in larger flocks which slowly sank to the bottom or were drawn by the vortices against the glass walls while the particles covered with oily fluid adhered.

If by the influence of light more spreading fluid is formed on the light side of the suspended particles than on the shaded side the suspended particles will go towards the light, that is, be posi-

[42] Chemical News, 1901, **84** : 174.

tively photodromic. Under the contrary supposition, they would go to the shaded side or be negatively photodromic.

205. **Destruction of Floccules.**—The destruction of the natural floccules is seen in the ordinary process of puddling earth or clay. It is also the result of violent agitation of water or of kneading or boiling, or, finally, to a certain extent, of freezing. All these agencies are employed by the workers in clay for the purpose of increasing the plasticity which depends essentially upon the finest possible condition of the material to be worked. As an illustration of this, Hilgard cites the fact that any clay or soil which is worked into a plastic paste with water, and dried, will form a mass of almost stony hardness. If, however, to such a substance one-half per cent of caustic lime be added, a substance which possesses in an eminent degree the property of coagulating clay, the diminution of plasticity will be obvious at once, even when in a wet condition. If now the mass be dried, as in the previous case, it is easily pulverized. This is an illustration of the effect of lime upon stiff lands, rendering them more readily pulverulent and tillable. The conversion of the lime into a carbonate in the above experiment by passing bubbles of carbonic acid through the mass while still suspended in water does not restore the original plasticity, thus illustrating experimentally the fact known to all farmers that the effect of lime on stiff soil lasts for many years, although the whole of the lime in that time has been converted into carbonate.

206. **Practical Applications.**—The practical application of this is, according to Hilgard, that the loosely flocculated aggregation of the soil particles is what constitutes good tilth. For this reason the perfect rest of a soil, if it is protected from the tamping influence of rains and the tramping of cattle, may produce a condition of tilth which cannot be secured by any mechanical cultivation. As an illustration of this, the pulverulent condition of virgin soils protected in a forest by the heavy coating of leaves may be cited. On the contrary, as pointed out by Hilgard, there are some kinds of soil in which a condition of rest may produce the same effect as tamping. These are soils which consist of siliceous silt without enough clay to maintain them in position

after drying. In such a case, the masses of floccules collapse by their own weight or by the least shaking, and fall closely together, producing an impaction of the soil. This takes place in some river sediment soils in which the curious phenomenon is presented of injurious effects produced by plowing when too dry, which is the direct opposite of soils containing a sufficient amount of clay and which are injured by plowing too wet.

It is further observed that the longer a soil has been maintained in good tilth, the less it is injured by wet plowing. This is doubtless, due, according to Hilgard, to the gradual cementation of the floccules by the soil water which fixes them more or less permanently.

Whitney believes that the arrangement of the grains, or the condition of flocculation in the soil, or the distance apart of the soil grains, is determined, to a large extent, by the potential on the surface of the grains; and he suggests that by changing this the exceedingly fine grains of silt and clay can be pulled together or can be pushed further apart, and so alter the whole texture of the land.

The action of alkaline carbonates in preventing flocculation, and thus rendering tillage difficult or impossible, is pointed out by Hilgard in the case of certain alkali soils of California. The soils which are impregnated with alkaline carbonates are recognized by their extreme compactness. The suggestion of Hilgard to use gypsum on such soils has been followed by the happiest results. This gypsum tends to render phosphates insoluble, and thus prevents loss by drainage, and yet leaves the plant food in a sufficiently fine state to be easily available for absorption.

207. Suspension of Clay in Water.—The suspension of clay in water and the methods of producing or retarding flocculation and precipitation have also been studied by Durham.[43]

In a number of tall glass jars fine clay is stirred with water, and the results of precipitation watched. In all cases it will be noticed that the clay rapidly separates into two portions, the greater part quickly settling down to the bottom of the jars, and the smaller part remaining suspended for a greater or less length of time.

[43] Chemical News, 1874, **30** : 57.

The power which water possesses of sustaining clay is gradually destroyed by the addition of an acid or salt; a very small quantity, for instance, of sulfuric acid, is sufficient to precipitate the clay with great rapidity. The ability to hold the clay in suspension in this case may be partially restored by neutralizing the acid. In solutions of sulfuric acid and sodium chlorid of varying strengths, suspended clay is precipitated in the order of the specific gravity of the solutions, the densest solutions being the last to clear up. This may be due to the greater viscosity of the denser liquids.

The power which water possesses of sustaining clay is gradually decreased by the addition of small quantities of certain salts and of lime.

208. Effect of Chemical Action.—Brewer[44] emphasizes the importance of chemical action in the flocculation of clays. As expressed by him the chemical aspects of the phenomena of sedimentation have either been lightly considered or entirely ignored. Brewer is led to believe that the action of clay thus suspended is analogous to that of a colloidal body. Like a colloid, when diffused in water, the bulk of the mass is very great, shrinking enormously on drying into a mass curiously like some organic colloids. He therefore concludes that clays probably exist in suspension as a series of hydrous silicates feebly holding different proportions of water in combination and having different properties so far as their behavior to water is concerned.

Some of them he supposes swell up in water much as boiled starch does, and are diffusible in it with different degrees of facility, and that the strata observed on long standing of jars of suspended clay represent different members of this series of chemical compounds which hold their different proportions of combined water very feebly and are stable under a very limited range of conditions.

These compounds are probably destroyed or changed in the presence of acids, salts and various other substances, and are stable only under certain conditions of temperature, those which exist at one temperature being destroyed or changed to other compounds at a different temperature.

[44] American Journal of Science, 1885, [3], **29** : 1.

209. Theory of Barus.—Brewer's hypothesis, however, is not in harmony with the demonstration of Barus, who proves that a given particle of clay has the same density in ether as in water.

The physical and mathematical aspects of sedimentation have also been carefully studied by Barus.[45]. The mathematical conditions of a fine particle suspended in a liquid and free from the influences of flocculation are described by Barus in the following equations.

If P be the resistance encountered by a solid spherule of radius r, moving through a viscous liquid at the rate x, and if k be the fractional coefficient, then $P = 6\pi krx$. Again, the effective part of the weight of the particle is $P' = \frac{4}{3}\pi r^3 (\rho - \rho')g$, where g is the acceleration of gravity and ρ and ρ' the density of solid particle and liquid, respectively. In case of uniform motion $P = P'$.

Hence $x = \frac{2}{9k} r^2 (\rho - \rho')g$ ..... (1).

In any given case of thoroughly triturated material the particles vary in size from a very small to a relatively large value; but by far the greater number approach a certain mean figure and dimension. An example of this condition of things may be formulated. To avoid mathematical entanglement let $y = Ax^{\frac{1}{2}}e^{-x^2}$ .. .. (2) where y is the probable occurrence of the rate of subsidence x. If now the turbidity of the liquid (avoiding optical considerations) be defined as proportional to the mass of solid material particles suspended in unit of volume of liquid, then the degree of turbidity which the given ydx particles add to the liquid is *caeteris paribus*, proportional to r^3ydx, where r is the mean radius. Hence the turbidity, T, at the outset of the experiment (immediately after shaking), is $T = T_0 \int_0^\infty r^3 ydx = T_0$, where equations (1) and (2) have been incorporated.

If the plane at a depth d below the surface of the liquid be regarded, then at a time after shaking the residual turbidity is

$$(3) \ldots\ldots T_d = T_0 \int_0^{\frac{d}{t}} r^3 ydx = T\left(1 - \left[1 + \frac{d^2}{t^2}\right] e^{\frac{d^2}{t^2}}\right)$$

The equation describes the observed occurrences fairly well.

The phenomena of stratification observed by Brewer are ex-

[45] American Journal of Science, 1889, [3], **37** : 122.

plained by Barus from the above formula: In proportion as the time of subsidence is greater, the tube shows opacity at the bottom, shading off gradually upward, through translucency, into clearness at the top. If, instead of equation (2), there be introduced the condition of a more abrupt maximum, if, in other words the particles be very nearly of the same size, then subsidence must take place in unbroken column capped by a plane surface which at the time zero coincides with the free surface of the liquid. Again, suppose one-half of the particles of this column differ in some way uniformly from the other half. Then at the outset there are two continuous columns coinciding, or, as it were, interpenetrating throughout their extent. But the rate of subsidence of these two columns is necessarily different, since the particles, each for each, differ in density, radius and frictional qualities, by given fixed amounts. Hence the two surfaces of demarcation at the time zero coincide with the free surface. In general, if there be n groups of particles uniformly distributed, then at the time zero n continuous columns interpenetrate and coincide throughtout their extent. At the time t, the free surface will be represented by n consecutive surfaces of demarcation below it, each of which caps a column, the particles of which form a distinct group.

From a further discussion of the mathematical condition under which the subsidence of the particles takes place, Barus is of the opinion that Durham's theory of suspension being only a lower limit of solution is rapidly gaining ground, yet without being attended with concise experimental evidence which will account for the differences in the rate of subsidence. On the contrary, Brewer's hypothesis of colloidal hydrates is more direct and should be subjected to experimental proof. The test shows that the particles retain their normal density, no matter how they are suspended or circumstanced. Their density in ether and water in other words is nearly the same.

Further, in the explanation of the phenomenon of sedimentation, the following principle may be regarded as determined; namely, if particles of a comminuted solid are shaken up in a liquid, the distribution of parts after shaking will tend to take place in such a way that the potential energy of the system of

solid particles and liquid, at every stage of subsidence, is the minimum compatible with the given conditions.

According to Barus it is necessary, in order to pass judgment on the validity of any of the given hypotheses, to have in hand better statistics of the size of the particles relative to the water molecule, than are now available. Inasmuch as the particles in pure water are individualized and granular, it is apparently at once permissible to infer the size of the particles from the observed rates of subsidence. His observations show that the said rate decreases in marked degree with the turbidity of the mixture. Hence the known formulæ for single particles are not rigorously applicable, though it cannot be asserted whether the cause of discrepancy is physical or mathematical in kind. It follows that special deductions must be made for the subsidence of stated groups of particles before an estimate of their mean size can fairly be obtained.

Rowland[46] reaches a closer approximation for the fall of a single particle by showing that the liquid, even at a large distance from the particle, is not at rest.

In the case of water, however, it is noticed that despite the large surface energy of the liquid, subsidence takes place in such a way that for a given mass of suspended sediment the surfaces of separation are a maximum. On the other hand, in case of subsidence in ether or in salt solutions, the solid particles behave much like the capillary spherules of a heavy liquid shaken up in a lighter liquid with which it does not mix. In other words, the tendency here is to reduce surfaces of separation to the least possible value, large particles growing in mass and bulk mechanically at the expense of smaller particles; in other words, exhibiting the phenomenon of flocculation.

210. **Practical Applications**—The action of certain soluble mineral substances in promoting flocculence has been taken advantage of in later times in the construction of filters for purifying waters holding silt in solution. In these filters the introduction of a small quantity of alum, or some similar substance, into the water usually precedes the mechanical separation of the flocculent mate-

[46] Proceedings National Academy of Science, 1892.

rial. In the same way the action of iron and other salts on sewage waters has been made use of in their purification and in the collection of the sewage material for fertilizing purposes.

METHODS OF SEPARATING SOIL PARTICLES.

211. Separation of the Soil Into Particles of Standard Size.—The agronomic value of a soil depends largely on the relative size of the particles composing it. The finer the particles, within a certain limit, in materials of practically the same chemical composition, the better the soil. The size of the particles may be estimated in three ways: (1) by passing through sieves of different degrees of fineness; (2) by allowing them to subside for a given time in water at rest; (3) by separating them in water moving at a given rate of speed. The first method is a crude one and is used to prepare in a rough way, the material for the second and third processes.

212. Separation in a Sieve.—The soil should be dry enough to avoid sticking to the fingers or to prevent agglutination into masses when subjected to pressure. It should not, however, be too dry to prevent the easy separation of any agglutinated particles under the pressure of the thumb or of a rubber pestle.

The sieve should have circular holes punched in a sheet of metal of convenient thickness to give it the requisite degree of strength. Sieves made of wire-gauze are not so desirable but it is difficult to get the finer meshes as circular perforations. Gauze seives cannot give a uniform product on account of the greater diagonal diameter of the meshes and the ease with which the separating wires can be displaced. It is convenient to have the sieves arranged *en batterie;* say in sets of three. Such a set should have the holes in the three sieves of the following dimensions, *viz.,*

1st sieve	2	millimeters diameter.
2nd "	1	millimeter "
3rd "	0.5	" "

Coarser single sieves may be used to separate the fragments above two millimeters diameter if such a further classification be desired. Each sieve fits into the next finer one and the separation of a sample into three classes of particles may be effected by a single operation. In most cases, however, it is better to conduct

each operation separately in order to promote the passage of agglutinated particles by gentle pressure with the thumb or with a rubber pestle. In no case should a hard pestle be used and the pressure should never be violent enough to disintegrate mineral particles.

There is much difference of opinion concerning the smallest size of particles which should be obtained by the sieve.

Most analytical processes prescribe particles passing a sieve of one millimeter mesh ($^1/_{25}$ inch). There is little doubt, however, of the fact that a finer particle would be better fitted for subsequent analysis by the hydraulic method.

For this purpose a sieve of 0.5 millimeter circular mesh is preferred.

213. Sifting with Water.—In soils where the particles adhere firmly the sifting should be done with the help of water. In such cases the soil is gently rubbed with a soft pestle or the finger in water. It is then transferred to the sieve or battery of sieves which are held in the water, and rubbed through each of the sieves successively until the separation is complete. After the filtrate has stood for a few minutes the supernatant muddy liquor is poured off, the part remaining on the sieve is added to it and the process repeated until only clean particles larger than 0.5 millimeter are left on the sieve. These particles are dried and weighed and entered on the note book as sand. The filtrate should be evaporated to dryness at a gentle temperature and when sufficiently dry be rubbed up into a homogeneous mass by a rubber pestle.

The sieve recommended by the Association of Official Agricultural Chemists for the preparation of fine earth for chemical analysis has circular openings $^1/_{25}$ inch (one millimeter in diameter.

Wahnschaffe directs that a sieve of two millimeters mesh be used in preparing the sample for silt analysis and that the residue, after the silt analysis is finished, which has not been carried over by a velocity of twenty-five millimeters per second, be separated in sieves of one millimeter and 0.5 millimeter meshes respectively.

Hilgard objects to leaving this coarse material in the sample during the process of churn elutriation on account of the attrition which it exerts and therefore directs that it be separated by sieve analysis before the elutriation begins.

214. Method of the German Experiment Stations.[47]—In this method an attempt is made to secure even a finer sieve separation than that already mentioned.

Sieves having the following dimensions are employed; sieve No. 1, square meshes 0.09 millimeter in size, diagonal measure 0.11 millimeter; sieve No. 2, square meshes 0.14 to 0.17 millimeter in diameter, diagonal measure 0.22 to 0.24 millimeter; sieve No. 3, square meshes 0.35 to 0.39 millimeter in diameter, diagonal measure 0.45 to 0.050 millimeter; finally a series of sieves one, two and three millimeters circular perforations.

Five hundred grams of the soil (in the Halle Station only 250) are placed in a porcelain dish with about one liter of water and allowed to stand for some time with frequent stirring, on a water bath. After about two hours, when the soil is sufficiently softened so that with the help of a pestle it can be washed through the sieve, the process of sifting is undertaken in the following manner: Sieve No. 3 is placed over a dish containing water, the moistened soil placed therein and the sieve depressed a few centimeters under the water and the soil stirred by means of a pestle until particles no longer pass through. After the operation is ended the residue in the sieve is washed with pure water and dried. The part passing the sieve is thoroughly stirred and then washed with water into sieve No. 2 and treated as before. The product obtained in this way is brought into sieve No. 1 and carefully washed. All the products remaining on each of the sieves are dried at 100° and weighed. The portion passing sieve No. 1 is either dried with its wash water or estimated by loss deducting from the total weight taken, the sum of the other weights obtained. If a more perfect separation of the first sieve residue be desired it can be obtained by passing it through sieves of the last series which may have meshes varying in size, *viz:* one, two, or three millimeters in diameter. Each sieve of the same class should have holes uniformly of the same size.

[47] Die landwirtschaftlichen Versuchs-Stationen, 1891, **38** : 309.

The sieve products are characterized as follows: The part passing a three millimeter sieve is called fine earth, while the part remaining is called gravel. The fine earth is separated into the following products: The part that passes through the three millimeters opening and is left by the two millimeters opening is called *Steinkies.* The product from the two millimeters opening and the residue from the one millimeter opening is called *Grobkies.* The product from the one millimeter opening and the residue on the sieve No. 3 is called *Feinkies.* The product from the sieve No. 3 and the residue from the sieve No. 2 is called *Grobsand.* The product from sieve No. 2 and the residue from sieve No. 1 is called *Feinsand.* The product from sieve No. 1 is called *Staub.* The dust can be further separated into *Staubsand* and *Thon.* For the examination of the clay the Kühn silt cylinder as modified by Wagner, is recommended. The cylinder has a diameter of eight centimters and a height of thirty centimeters, and is furinshed with a movable exit tube reaching to its bottom. Detailed directions for this separation will be given further on. (Paragroph 220).

215. General Classification of the Soil by Sieve Analysis.—The classification recommended by the German chemists is satisfactory but the following one is more simple. All pebbles, pieces of rock, sticks and roots should be picked out of the sample, and the residue of coarse matter be separated by a two millimeters circular mesh sieve, dried at 105° and weighed. The result should be entered as pebbles and coarse sand.

The finer sand may be separated with a sieve of one millimeter circular openings.

The still finer sand is next separated with the sieve of 0.5 millimeter circular openings as indicated above.

The sample may now be classified as follows:

1. Coarse pebbles, sticks, roots, etc., separated by hand.
2. Pebbles and coarse sand not passing a two millimeters sieve.
3. Sand not passing a one millimeter sieve.
4. Fine sand not passing a 0.5 millimeter sieve.
5. Fine earth passing a 0.5 millimeter sieve.

216. Classification of Orth.[48]—As fine earth are reckoned those

[48] Berichte der deutschen chemischen Gesellschaft, 1882, **15** : 3025.

particles which range from 0.02 to 0.05 millimeter; as fine sand the groups from 0.05 to 0.2 millimeter; as medium sized sand those ranging from 0.2 to 0.5 millimeter and for large grained sand those particles ranging from 0.5 to 2 millimeters in diameter. Particles over two millimeters form the last classification.

217. Nomenclature of Silt Particles.—It is evident from the foregoing discussion that much confusion exists regarding the terms employed to designate the different classes of silt particles obtained by mechanical analysis. Even the classes formed by determining approximately like diameters are differently designated by different investigators. It would be advisable to reach some international agreement respecting the characters of these divisions, leaving to each country the choice of an appropriate name. Such an agreement might be secured through the International Congress of Applied Chemistry.

The chaotic condition of the nomenclature at the present time has been studied by Atterberg.[49]

Especially is it desirable to have some systematic method of describing the fine sand as it merges into clay. Judged by relations to the penetration of rootlets and water the limit of 0.2 millimeter diameter separates porous from water holding particles; while 0.02 millimeter is the limit for coagubility of the fine particles by a solution of sodium chlorid and 0.002 millimeter the limit of marked molecular movement. Particles smaller than 0.02 millimeter cannot be seen by the unarmed eye. The hair roots of plants cannot penetrate sand finer than 0.02 millimeter diameter.

The decimal system of division has the merit of simplicity and if agreed upon internationally would bring order into what is now great confusion.

The suggested groups of particles with their names in three languages are represented as follows:

Diameter.	Name.		
	Swedish.	German.	English.
From 2.0 to 0.2 mm.	Sand	Sand	Sand
" 0.2 " 0.02 "	Mo	Feinsand	Fine sand
" 0.02 " 0.002 "	Lättler	Lehm	Silt
" 0.002 " finer.	Ler	Thon	Clay

[49] Chemiker Zeitung, 1905, 29 : 15.

One objection to the plan of grouping by limiting diameters is found in the irregular shape of the particles, which would make them eligible to more than one class, as they might be judged by their long or short diameters. Almost any uniform plan of designation would be better than the present system, in which each investigator uses a separate classification.

SEPARATION OF THE EARTH PARTICLES BY A LIQUID.

218. **Methods of Silt Analysis.**—The further classification of the particles of a soil passing a fine sieve can best be effected by separation in water. The velocity with which the current moves or with which the particles subside will cause a separation of the particles into various sizes. The slower the velocity the smaller the particles which are separated. There is, however, a large and important constituent of a soil which remains suspended in water, or in a state of seeming solution. This suspended matter would still be carried over by a current of water moving at a rate so slow as to make a subclassification of it impossible. This suspended matter passing off at a given velocity may be classed as clay, and it consists in fact chiefly of the hydrated silicate of alumina, or other particles of equal fineness. The laws which govern its deposit have already been discussed.

The apparatus which have been used for silt analysis may be grouped into four classes.

(1) Apparatus depending on the rate of descent of the particles of a soil through water at rest. The apparatus for decanting from a cylinder or a beaker belong to this class.

(2) Apparatus which determine the rate of flow by passing the liquid through a vessel of conical shape. The system of Nöbel is a good illustration of this kind of apparatus.

(3) Apparatus in which the elutriating vessel is cylindrical and the rate of flow determined by a stop-cock or pressure feed apparatus. The system of Schöne represents this type.

(4) Apparatus in which the above system is combined with a device for mechanically separating the particles and bringing them in a free state into the elutriating current. The system of Hilgard is the type of this kind of apparatus.

In practice the use of cylindrical apparatus with or without me-

chanical stirring and the method by decantation have proved to be the most reliable and satisfactory procedures. Between the beaker and churn methods of separation there is little choice in regard to accuracy. The large number of samples which can be examined simultaneously and the freedom from mechanical difficulties render the method depending on simple subsidence more practical. Which is the superior method respecting accuracy is a question on which the opinions of experienced analysts are divided. The various processes will be described in the order already mentioned.

219. Methods Depending on Subsidence of Soil Particles.—The simplest method of effecting the further separation of the soil particles is without doubt that process which permits them to fall freely in a liquid sensibly at rest. The practical difficulties of this method consist in the trouble of securing a perfect separation of the particles, in preventing flocculation after division and in avoiding currents in the liquid of separation.

For the disintegration of the soil particles in this method boiling and wet pestling are the only means employed. The flocculation of the separated particles may be partially prevented by adding a little ammonia to the water employed. The author has also tried dilute alcohol as the separating liquid but the results of this method are not yet sufficiently definite to find a place in this manual. Evidently the practical impossibility of avoiding convection currents prevents the use of water at a high temperature for this separation although the tendency to flocculation almost disappears as the temperature approaches 100°. The general method of avoiding the errors due to flocculation in the subsidence method consists in repestling the deposited particles and thus subjecting them as often as may be necessary to resedimentation. The principles are well set forth by Osborne,[50] who states that when a soil is completely suspended in water by vigorous agitation, particles of all the sizes present are to be found throughout the entire mass of liquid. When subsidence takes place, the larger particles will go down more rapidly than the smaller ones, but some of the small

[50] Connecticut Agricultural Experiment Station, Annual Report, 1886, 141.

particles that are near the bottom will be deposited sooner than some of the larger ones which have a much greater distance to travel. Thus, independently of the fact that the larger particles in their descent are somewhat impeded by the smaller, the smaller being at the same time somewhat hastened by the larger, the sediment that reaches the bottom at any moment is a more or less complex mixture of all the mechanical elements of the soil. The liquid, however, above this sediment at the same moment will have completely deposited all particles exceeding certain dimensions of hydraulic value, determined mainly by the time of subsidence.

If now the aforesaid first sediment be suspended in pure water, and allowed to subside for the same time as before, the larger part of it will be again deposited, but some will remain in suspension, consisting of a considerable part of the finer matter of the first sediment. By pouring off these suspended particles with the water and agitating the sediment again with clear water as before, another portion of fine particles will be suspended and may be decanted from it. On continuing this process of repeated decantations it will soon be found that the soil has been separated into two grades.

It is evident that in this way a separation can be made, but it is perhaps not so clear that such a separation would be sharp enough for the purpose of a mechanical soil analysis. If, for instance, the separation is to be made at 0.05 millimeter diameter, it is evident that by repeated decantations all below 0.01 millimeter can be washed out of that above 0.05 millimeter, but it may not appear so probable that all below 0.045 millimeter can be removed without removing some above 0.055 millimeter.

Such a result may be easily attained, however, if the following principle be adhered to:

Make the duration of the subsidence such that the liquid decanted the first few times shall contain nothing larger than the desired diameter. Then decant into another vessel, timing the subsidence so that the sediment shall contain nothing smaller than the chosen diameter. This can not be done without decanting much that is larger than the chosen diameter, but the greater part

of the particles greater and less than the chosen diameter can be removed and an intermediate product obtained, the diameters of whose particles are not very far from that desired.

If this intermediate portion be again subjected to the same process, two fractions may be separated from it, one containing particles larger than the chosen diameter and another containing particles smaller than this diameter, while a new intermediate product will remain which is less in amount than that resulting from the first operation. By frequent repetitions of this process this intermediate product can be reduced to a very small amount of substance the particles of which have diameters lying close to the chosen limit and may then be divided between the two fractions.

The principles of the separation described by Osborne set forth with sufficient clearness the purposes to be achieved by the analysis, and the method in detail will be found further along.

SEPARATION OF SOIL PARTICLES BY DECANTATION.

220. Kuehn's Silt Cylinder.—A simple form of apparatus for the determination of silt by the sedimentation process is the one described by Kühn.[51]

The cylinder should be about 30 centimeters high with a diameter of 8.5 centimeters. At the lower end of the cylinder five centimeters from the bottom it carries a tube 1.5 centimeter in diameter closed by a rubber stopper, the inner end of which must be flush with the inner wall of the cylinder.

In carrying out the process 30 grams of sifted soil (two millimeter mesh sieve) are boiled with water for an hour and after cooling the soil and water are washed into the separating cylinder previously, filled with water to a depth of 28 centimeters. With a smooth wooden stick the contents of the cylinder are stirred vigorously for one minute.

After standing for ten minutes the stop-cock is opened and the water with its suspended matter allowed to flow out, a sample of a given volume being saved.

[51] Steinrede, Anleitung zür mineralogischen Bodenanalyse, 1889, 9-13.
Die landwirtschaftlichen Versuchs-Stationen, 1893, **42** : 153.
König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, Second Edition, 8.

The cylinder is then again filled with water and the process is continued until the water drawn off is practically clear. The various samples which have been taken are united, thrown on a filter, and the mass remaining on the filter, mixed and subjected to microscopic examination.

The fine particles having been separated in this way in one of the modifications of the method, the next coarser grade of particles is separated by repeating the process and allowing five minutes for subsidence.

By these two operations it is considered that the clay is entirely removed. The residue remaining in the cylinder is dried and weighed. The relative proportions of clay and residue in the sample are thus determined.

The residue is then separated into two portions by sieves of one millimeter and 0.5 millimeter mesh. A third separation with a sieve of 0.25 mm. mesh is also sometimes made.

The soil is thus separated into the following parts:

1. By the first sifting coarse quartz larger than two millimeters diameter.
2. Fine quartz two millimeters, to one millimeter diameter.
3. Coarse sand one millimeter, to 0.5 millimeter diameter.
4. Fine sand finer than 0.5 millimeter diameter.
5. Silt, clay, humus, etc., separated by the water.

221. Knop's Silt Cylinder.—The cylinder recommended by Knop[52] is essentially that of Kühn being furnished with four lateral tubes instead of one (Fig. 31). The distance between each tube is ten centimeters.

The sample of soil, from 25 to 30 grams, after passing a two millimeter mesh sieve, and long boiling, is washed through a series of sieves of the following diameters of mesh respectively; *viz.*, one millimeter, 0.5 millimeter, 0.25 millimeter, and 0.1 millimeter. The part which passes the finest sieve is placed in a Knop's cylinder, the cylinder filled with water one decimeter above the upper tube and well shaken. The cylinder is allowed to rest for five minutes when the upper cock is opened and the water drawn off. After five minutes more the next tube is opened and so on with equal intervals for the three upper tubes.

[52] Konig, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, Second Edition, 10.

The operation is repeated with fresh water until the water drawn off is clear. Finally the lowest tube is opened and all the water poured off of the sandy residue. The remaining material is dried and weighed and the weight of silt carried over as determined by difference.

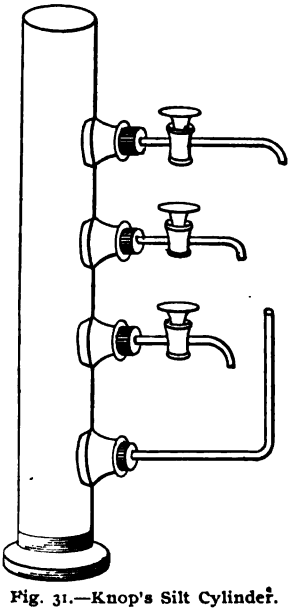


Fig. 31.—Knop's Silt Cylinder.

222. Siphon Silt Cylinder.—Instead of the tubulated cylinder one furnished with a siphon (Fig. 32) can be employed.[53]

It should be about 40 centimeters high and six centimeters internal diameter. From 20 to 30 grams of the well boiled fine earth is placed in the cylinder and then water added until there is but a small space between it and the stopper when the latter is inserted.

The cylinder is marked at exactly 200 millimeters below the surface of the water with a narrow strip of paper at *a*, stoppered, inverted and well shaken. The cylinder being again placed in normal position the soil particles under the influence of gravity tend

[53] Wahnschaffe, Anleitung zur wissenschaftlichen Bodenuntersuchung, 24.

to sink with greater or less rapidity according to their size. The siphon *a b c* is filled with water, the cock at *c* closed and the opened end *a* placed in the cylinder A just at the mark 200 millimeters below the surface of the water, and the water thus transferred to B when desired. If the cylinder is allowed to stand for

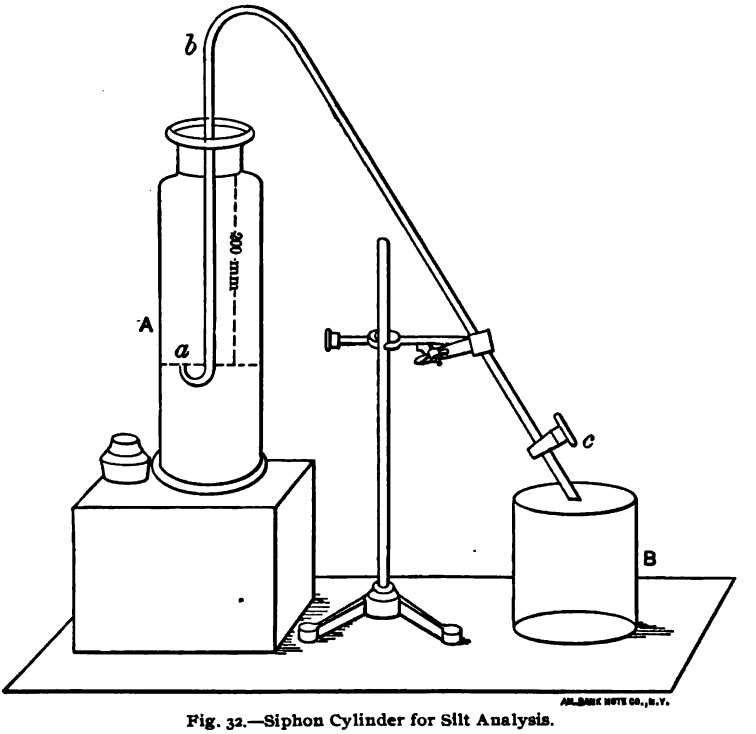


Fig. 32.—Siphon Cylinder for Silt Analysis.

100 seconds the particles of more than two millimeters hydraulic value per second will have fallen below the open end of the siphon. If allowed to stand 1,000 seconds the hydraulic value of the particles will be 0.2 millimeter per second. Whatever the number of seconds may be, the operation is continued until the water removed is practically clear. The open end of the siphon *a* should be bent upwards so that no disturbing current may bring the particles below the line into the liquid discharged into B.

While the results obtained by this method are satisfactory as compared with other similar processes it cannot be highly rec-

ommended because of the time and trouble required to get a complete separation and by reason of the difficulty of collecting the separated silt.

223. Wolff's Method.[54]—As modified by Wolff the Knop process is conducted as follows: From 20 to 30 grams of fine earth are boiled with water and then the entire mixture is passed through sieves with openings of 1, 0.5, 0.25, and 0.1 millimeter in diameter, respectively. The finest part is mixed with water to a height of 18 centimeters in a cylindrical vessel 20 centimeters high and having a capacity of one liter and thoroughly agitated, after which it is left to rest, and finally the turbid liquid is drawn off with a siphon, the bottle refilled with water, agitated, and left to rest, and the process repeated three times or as long as the water carries any suspended matter after a definite time.

Wolff proposes for the first three periods of rest one hour, for the second three, a half an hour, for the third three, a quarter of an hour, and for the fourth three, five minutes.

224. Moore's Modification of Knop's Method.[55]—The sample of soil boiled rapidly with water until the lumps are disintegrated and the clayey portions separated from the sand, is first passed through sieves as described above except the finest. The weight of the particles remaining on the sieves is determined, and that of the portion lost passing through, which is known as fine earth is determined by differnce. The last named portion constitutes the material for all subsequent operations of mechanical analysis.

The sediment and water passing through the 0.25 millimeter sieve are placed in a glass cylinder 53 centimeters long and 37 millimeters in internal diameter. The cylinder is closed at the bottom and is provided with a lateral tube inserted six centimeters above the bottom. Three other lateral tubes are inserted at intervals of ten centimeters above the first tube, and a ring is etched into the cylinder ten centimeters above the uppermost tube. The

[54] Wolff, Chemische Untersuchung landwirtschaftliche Stoffe, Berlin, Third Edition, 10.
König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, 9.

[55] Tenth Census, 8 : 872-3.

lateral tubes are closed with rubber tubes compressed by spring clips. The sediment being placed in the cylinder, water is added to the mark or ring, the cylinder closed with a rubber stopper, and vigorously shaken until the contents are thoroughly mixed. It is then placed upright, the stopper removed, and after standing undisturbed for five minutes the clip on the uppermost tube is opened and the water allowed to flow into a beaker. After five minutes further standing, the second clip is opened and the water drawn off into the same beaker; in the same manner the water is drawn off from the other tubes at intervals of five minutes until the level of the lowest tube is reached. The cylinder is then refilled with water to the mark, thoroughly shaken after inserting the stopper and the water again drawn off at intervals of five minutes, as before; the operation being repeated until the water drawn off is almost free from turbidity. The sediment remaining in the cylinder from this process of washing by subsidence is termed by Knop, fine sand, the material flowing off in suspension in the wash waters, dust, and the process of separation by Knop's original method ends here.

In order to remedy the imperfect separation into definite particles secured by the above method, Moore used the following method:

The fine sand from the first series of subsidences is placed in a separate vessel, the washings are allowed to remain undisturbed for twelve hours, the turbid liquid decanted and the sediment returned to the cylinder. Water is then added to the mark, the whole shaken, and the liquid drawn off at intervals of five minutes, as in the first series. The sediment from this operation is placed in a separate beaker, the washings returned to the cylinder, and again allowed to subside as before; the sediment from this second subsidence is added to that from the preceding operation, and the washings again returned to the cylinder, the operation being repeated as long as any sediment can be obtained from renewed treatment of the washings; the final washings are then placed in a separate vessel for subsequent microscopic measurements.

The collective sediments from the last series of operations are then returned to the cylinder and allowed to subside with fresh

additions of water, as in the case of the first series; the fine sand thus obtained being added to that from the first series, and the washings being collected in a large beaker. The latter is left at rest for twelve hours, and the sediment returned to the cylinder and treated as before until no further separation can be effected. The fine sand resulting from all of these operations is then dried, ignited and weighed; the weight of the portion removed by the washing being determined by difference, as it is, owing to its excessively slow rate of subsidence, found impracticable to collect it for direct weighing. The size of the particles of fine sand is then determined by micrometric measurement. Similar measurements are made on the material obtained by long subsidence from the washings from the foregoing operations. The average diameter of the largest particles should not exceed 0.01 millimeter.

225. **Statement of Results.**—The results of the analyses on three soils from the localities indicated in the table, and the method of stating them, are given in the following table:

	New Milford Conn., per cent.	Clarksville, Tenn., per cent.	Granville, N. C., per cent.
Particles larger in diameter than 3.0 millimeters	8.55	0.32	0.23
Particles of diameter from 3.0 millimeters to 1.0 millimeter	4.96	0.45	15.04
Particles of diameter from 1.0 millimeter to 0.5 millimeter	4.43	0.96	33.43
Particles of diameter from 0.5 millimeter to 0.25 millimeter	11.86	1 25	18.82
Particles of diameter from 0.25 millimeter to 0.01 millimeter	60.54	61.58	23.59
Particles smaller in diameter than 0.01 millimeter	9.66	35.44	8.89
Total	100.00	100.00	100.00

226. **Claussen's Apparatus.**—The apparatus is constructed on the principle of that of Bennigsen, given further on, but is capable of giving more exact results.[56]

It is composed of two pieces, a pear-shaped bulb and a long neck. The long neck of the bulb as described in Bennigsen's

[56] Wahnschaffe, Anleitung zur wissenschlaftlichen Bodenuntersuchung, 28. Illustrirte landwirtschaftliche Zeitung, 1889 : 29.

method has a diameter of 2 cm. for 75 cm., and is then drawn out into a smaller tube 25 cm. long and 11 mm. diameter. The bulb and long stem are joined together by a heavy rubber band.. The sample of air-dry earth which has passed a 2 mm. mesh sieve, is placed in the pear-shaped bulb of the apparatus and boiled for half an hour with water. About 30 grams of the fine earth are used and during the boiling the flask is frequently shaken. After cooling the bulb is filled almost full of water and the long stem closed at the lower end with a rubber stopper and filled with water, is fixed in place by the rubber band. After repeated shakings the whole apparatus is quickly inverted and the solid contents of the bulb begin to descend through the long neck. The sand and clay are fairly well separated during the descent and the relative quantities of fine and coarse particles are measured by the divisions on the lower constructed portions of the tube. The tube may now be separated from the bulb, its upper end closed by the finger, the stopper removed from the end containing the separated particles, and these allowed to run out in portions as nearly the same size as possible as in the manipulation of a pipette. The several portions are then dried and weighed. As in the preceding case it is evident that this process can give at best only an approximate separation.

227. **Method of Gasparin.**—The method of Gasparin only gives a very primitive separation of the various components of the earth according to their fineness.[57] It is conducted as follows:

Ten grams of sifted earth are put into a beaker, water is added and strongly agitated; after five minutes the water is decanted into another vessel, the first vessel is filled anew with water, agitated, decanted, and this process is repeated until the liquid remains perfectly clear. Only two portions are weighed, *i. e.*, the pebbles which remain in the sieve and the coarse sand which remains in the beaker; while the argillaceous portion drawn off with the water is determined by the difference.

228. **The Italian Method.**—The following modification of Gasparin's process is practiced by the Italian chemists:[58]

Twenty grams of earth are passed through a sieve having open-

[58] Encyclopédie chimique, **4** : 138.
Stazioni sperimentali agrarie Italiane, 1889, **17** : 672.

ings of one millimeter in diameter, then the sifted part is mixed with 100 cubic centimeters of water in a 200 cubic centimeter beaker and left to rest for some hours, strongly agitated, and after ten seconds the turbid liquid is poured into another vessel of half a liter capacity. This manipulation is repeated until the liquid is clear.

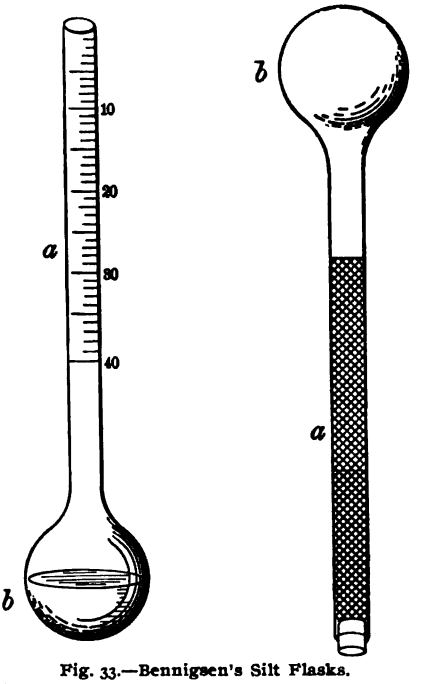


Fig. 33.—Bennigsen's Silt Flasks.

The decanted liquid is thoroughly agitated, then left to stand until the movement shall be completely arrested, after which the supernatant liquid is poured into another vessel holding two liters. To the residuum is added more water; it is agitated, decanted, and this process is repeated until the water is no longer turbid.

229. **Method of Bennigsen.**—The silt flasks recommended by Bennigsen[59] are shown in Fig. 33.

[59] Wahnschaffe, Anleitung zur wissenschaftlichen Bodenuntersuchung, Second Edition, 28.

The glass flask *b* carries a long cylindrical neck *a* the upper part of which is graduated in cubic centimeters. Ten grams of the fine soil are shaken with water in the flask, the neck of which is closed with a rubber stopper. The flask is then inverted bringing the soil and the water into the neck. The flask in hung up and sedimentation is assisted by imparting a pendulous motion to the neck for ten minutes. This manipulation results in the sedimentary action due to gravity being aided by a slight centrifugal force. After an hour the soil particles have separated into a corse layer below and a fine layer above, as indicated by the different shading on the neck of the inverted flask. The relative volumes of the two layers are then read off in cubic centimeters. While this method may be useful in helping to form a speedy judgment concerning the character of a soil it can lay no claim to being an accurate method of silt separation.

230. **Method of Osborne.**—In the foregoing paragraphs the methods of silt separation by subsidence as practiced in different countries have been outlined. The good points of the various methods are combined in the process as carried out by Osborne. The general principles on which this process rests have already been outlined. The details of this method will be given with sufficient minuteness to make its practice possible by all analysts.

Selecting the Sample.—Several pounds of air-dried, fine earth are secured by passing the soil through a sieve, the holes of which are three millimeters in diameter.

Sifting.—Thirty grams of the above fine earth are stirred with from 300 to 400 cubic centimeters of water and then thrown successively upon sieves with circular holes of 1, 0.5, and 0.25 millimeter diameter respectively. By means of successive additions of water and the use of a camel's hair brush, all the fine material is made to pass through the sieves and these at the last are agitated under water in a shallow dish in such a way that the soil is immersed. The finest sieve should be well wet with water on its lower surface just before using. The finest particles which render the water turbid are easily washed through. The turbid water is kept separated from the clear water which comes off with the last portions that pass the sieves. The turbid water usually does not amount to more than one liter.

Elutriation.—The elutriation should be carried on so as to secure three grades of silt; the diameters of the particles ranging in the first grades from 0.25 to 0.05 millimeter, in the second grade from 0.05 to 0.01 millimeter, and in the third grade from 0.01 millimeter to the impalpable powder. The term sand is applied to the first grade, silt to the second, and dust or dust and clay to the third. (After the turbid liquid from the sifting has stood a short time it is decanted from the sediment and after standing until a slight deposit is formed, is again decanted and the sediment examined with a microscope.) If sand be present, the subsidence of the turbid liquid is continued until no more sand is deposited. As the sand subsides rapidly there is no difficulty in altogether freeing the liquid first decanted from this grade of particles. The sediment thus obtained contains all the sand, a part of the dust and much silt. As only dust and the finest silt render the water turbid the sediment is stirred a few times with a fresh quantity of water and decanted after standing long enough to let all the sand settle. (When the water decanted is free from turbidity, the last portions of the soil passing through the sieve with clear water are added to the sediment and the decantations continued so as to remove most of the silt.) When no more silt can be easily removed from the sediment without decanting sand, the decantations are made into a different vessel and the subsidences so timed as to remove as much of the silt as possible. By using a little care, at least three-quarters of the sand are thus obtained free from silt. The rest of the sand is mixed with the greater part of the silt which has been decanted into the second vessel. The size of the smallest particles in this vessel is determined with the microscope, to make sure that its contents are free from dust as they usually will be if, after settling for a few moments, they leave the water free from turbidity.

The soil is thus separated into three portions, one containing sand, one sand and silt, and the other silt, dust, and clay. The sand and silt are separated from each other by repeating the subsidences and decantations in the manner just described.

In this way there is removed from the sediment, on the one hand, a portion of silt free from sand and dust, and on the other hand a portion of sand free from silt. Thus is obtained a second

intermediate portion consisting of sand and silt, but less in amount than the first and containing particles of diameters much more nearly approaching 0.05 millimeter. By repeating this process a few times, this intermediate portion will be reduced to particles whose diameters are very near 0.05 millimeter and which may be divided between sand and silt, according to judgment. The amount of this is usually very small. As soon as portions are separated, which the microscope shows to be pure sand or pure silt, they are added to the chief portions of these grades already obtained.

The same process is applied to the separation of silt from dust. When all the silt has been removed from the dust and clay, the turbid water containing the dust and clay is set aside and allowed to settle in a cylindrical vessel for twenty-four hours. The vessel is filled to a height of 200 millimeters. According to Hilgard, the separation of the dust from clay during a subsidence of twenty-four hours, will give results of sufficient accuracy, although the clay then remaining suspended will not be entirely free from measurable fine particles up to 0.001 or 0.002 millimeter diameter.

Small beakers and small quantities of distilled water are used at first for the decantations, as thus the duration of subsidence is less and more decantations can be made in a given time than when larger quantities of water are employed. Beakers of about 100 cubic centimeters capacity are convenient for the coarser grades, but it is necessary to use larger vessels for the fine sediments from which turbid water accumulates that cannot be thrown away, as may be done with the clear water, from which the coarse sediments settle out completely in a short time.

It is best to keep the amount of water as small as possible in working out the dust since loss is incurred in using too large quantities.

It is also necessary in most cases to subject the various fractions obtained during elutriation, to careful kneading with a soft rubber pestle so that the fine lumps of clay may be broken up and caused to remain suspended in the water. This treatment with the pestle should be done in such a way as to avoid as far as possible all grinding of the particles, the object being merely to pul-

verize the minute aggregations of clay and extremely fine particles which always form on drying a sample of soil after removing it from the field.

Measurement of the Particles.—To determine the size of particles in suspension, a small glass tube is applied to the surface of the liquid in such a way as to take up a single drop which is transferred to a glass slide. This drop will contain the smallest particles in the liquid.

To obtain a sample of the coarsest particles the liquid is allowed to stand long enough to form a very slight sediment and a portion of this sediment is collected with a glass tube.

To determine the diameter of the particles in a sediment it is stirred vigorously with a little water and the pipette at once applied to the surface of the water. On decanting the greater part of the sediment, the large particles remain at the bottom of the beaker and may be easily examined.

Time.—The time required to make the separations, above described, is about two hours for each, so that an analysis including the siftings, is made in five or six hours, exclusive of the time necessary for collecting the dust and separating the clay, for which a subsidence of 24 hours is allowed.

Weighing the Sediments.—The sediments are prepared for weighing by allowing them to subside completely, decanting the clear water as far as possible, rinsing them into a weighed platinum dish and igniting. The dish is cooled in a desiccator, and the ignited sediments are generally very hygroscopic.

Effect of Boiling.—The analyses show a very decided increase in the particles smaller than 0.01 millimeter diameter at the expense of coarser particles as the result of boiling. The surfaces of the coarser particles are seen to be polished and of a lighter color than those not boiled. The surfaces of the unboiled particles are coated with a film of fine material probably cemented to them by clay. When these coarse particles which have not been boiled, are violently stirred with water for a short time, no fine particles are detached from them; and a careful examination under the microscope fails to reveal in any of the sediments more than an occasional grain exceeding the 0.05 millimeter limit by so much as 0.01 millimeter, or the 0.01 limit by as much as 0.005

millimeter. It would, therefore, appear that these small particles thus set free by long boiling are really a part of the larger ones and should be treated as such in a mechanical analysis of these soils.

231. **The French Method.**—The consulting committee of the agricultural experiment stations and agricultural laboratories preface the description of the methods of mechanical analysis with the assumption that the soil is essentially formed of four elements, *viz.*, sand, clay, lime and humus. They reject the methods originally proposed by Gasparin and Masure and propose in their place the process described below.

The Schloesing method[60] as practiced by the French agricultural chemists[61] differs essentially from those already described in attempting to first free the silt from carbonatees and organic matter. It is conducted as follows:

One kilogram of the soil previously dried in the air, is passed through a sieve of five millimeter mesh. The agglomerated particles of earth are broken up by the hand. The pebbles and parts not passing through the sieve are weighed. The pebbles are then treated with hydrochloric acid until all effervescence is over. The insoluble part is dried and again weighed. The difference in weight gives the quantity of calcium carbonate contained on the external surface of the pebbles. The earth which passes the sieve of five millimeters mesh is next passed through a sieve having ten meshes to the centimeter. The masses on the sieve are broken up with the hand or with a soft pestle, in such a manner as to separate the fine agglomerated particles. The material which remains upon the sieve after being dried at 100°, is weighed. This gives the coarse sand. This is treated with hydrochloric acid as were the pebbles before, washed and the residue dried and weighed. The difference in weight gives the quantity of calcium carbonate adhering to the surface of the coarse sand.

The mechanical analysis is continued with the matter which has passed the sieve with ten meshes to the centimeter and which consists of the soil, properly so-called. Ten grams of this are dried at 100° until no further loss takes place and the moisture thus de-

[60] Encyclopédie chimique, 4 : 135 et seq.

[61] Annales de la Science agronomique 1891, 1, 2 fasicule : 250 et seq.

termined. Another 10 grams are placed in a capsule with a flat bottom, and from nine to ten centimeters in diameter. The earth is moistned with a small quantity of water in such a way as to make a paste. This paste is rubbed up with the finger in from 15 to 20 cubic centimeters of water. Ten seconds after the stirring is completed the supernatant liquid is poured into a precipitating jar of about 250 cubic centimeters capacity, taking great care not to allow any particles to pass over which have been deposited during that time. This operation is repeated in the same way waiting about ten seconds each time before decanting, until the decanting liquor is almost perfectly clear. In this way the particles of different degrees of fineness are separated. The decanted portions contain the fine sand and clay. The remaining portion contains the coarse sand. This last part is dried, being kept at 100° until it has a constant weight. It is afterwards treated with dilute nitric acid to dissolve the calcium carbonate. When the carbonate is abundant, it is sufficient to determine it by difference which is done by washing the material, drying and weighing. But when the proportion of carbonate is very small and in consequence when its exact determination acquires a greater importance, it is better to determine the lime directly. For this purpose the part soluble in dilute nitric acid is collected, treated with ammonia and acetic acid and precipitated with ammonium oxalate. Details of this operation will be given in another part of this manual.

In regard to the matter which is insoluble in nitric acid, it is composed chiefly of silica or silicates, and sometimes also of vegetable débris. The vegetable matter is determined by the incineration of the material which has been previously dried. The loss of weight gives the proportion of vegetable or organic débris contained in the soil and of combined water.

The portion which has been decanted, the volume of which should not exceed 500 cubic centimeters, is treated with nitric acid until effervescence ceases. It is then left to digest for some time, in order to permit the whole of the carbonate to dissolve. It is next thrown upon a smooth filter about one decimeter in diameter. After filtration it is washed to secure the complete elimination of

the soluble lime salts. The lime is determined in the filtered liquid.

The insoluble portion contains the fine sand, the clay and humus bodies. In order to separate the three elements the precipitate which was received upon the filter, is detached with water, the filter is broken and all its contents washed through. The volume of wash water is made up to 200 cubic centimeters; two or three cubic centimeters of ammonia are added and the whole left to digest for two or three hours. The volume of the liquid is then made up to one liter with distilled water, vigorously shaking in such a way as to put all the matter in suspension. It is then left to settle for 24 hours. At the end of this time the supernatant liquid is decanted by the aid of a siphon. To the residue are added two cubic centimeters of ammonia and one liter of water. The matter is again brought into suspension and allowed to settle for 24 hours. The supernatant liquid is again decanted with a siphon, and added to the liquid previously removed. For ordinary soils two decantations are generally sufficient but when the soils contain a large quantity of clay it is convenient to decant three or four times. By an examination of the supernatant liquid it is easy to tell if the washings have been sufficiently prolonged. The decanted liquors contain the organic matter and that which it is convenient to call clay, which is constituted of very fine particles of sand and colloidal clay which play, in arable soil, a rôle somewhat like that of cement.

These matters are estimated in the following manner: The liquor is first treated with nitric acid and the clay and the humic matters are precipitated together. They are collected upon a smooth filter one decimeter in diameter and washed with water. By means of a washing bottle all the solid matters which have stuck to the sides of the filter are finally collected in the bottom of it. Since the last washings pass the filter very slowly, they can be removed after the complete deposition of the matter they contain, by means of a pipette. When all the liquid is removed the filter is placed upon blotting paper, great care being taken to avoid desiccation, having in view only the elimination of the excess of humidity. The folds in the filter are then carefully smoothed out with the finger. The matter which has collected

upon the filter is then removed completely with a washing bottle, placed in a dish and dried at 100° and weighed. After weighing, the mass is incinerated in a muffle in order to destroy the humic bodies. The difference in weight before and after incineration, gives the total weight of the humic bodies and since the diminution in weight comprises not only the weight of the humic bodies, but also the weight of the combined water which is lost during the process of incineration, there should be subtracted from the total loss of weight ten per cent of the weight of the residual mineral matter, which represents the water of composition of the hydrated silicate. In this way the two chief cementing bodies of the soil are determined.

232. **Statement of the Analysis.**—Schloesing in his orignial paper[62] recommends that the results of analysis be computed to 1,000 grams of soil. The data of the analysis and the method of arrangement are illustrated by the following example.

The physical examination of the earth having been completed as above, the results can be tabulated on a quantity of soil equivalent to 1,000 grams of dry earth, as follows: Digest in water, thoroughly work by hand, sift, and pass through sieve one millimeter mesh by aid of water.

		Grams.
Dry residue, 55 grams, contains	Pebbles	21
	Gravel	33
	Organic débris	1
Sifted earth by difference, 1000–55 =		945
		1000

The water content of the homogeneous paste is 27 per cent. Then 945 grams of the dry sifted earth correspond to 1294.5 of paste.

The analysis, therefore, should be carried on upon this weight, or some aliquot part say 0.01 thereof; *viz.*, 12.945 grams.

			Grams.
12.945 grams of paste after successive kneadings and decantations furnish dry:	1st.—Coarse sand dry giving by treatment with acid and ignition.	Noncalcareous sand	3.05
		Calcareous sand	1.19
		Organic débris	0.08
	2nd.—Fine elements decanted with the water, their weight calculated by difference, 9.45 − 4.32 = 5.1_3 grams.		

[62] Encyclopédie chimique. 4 : 155 et seq.

Treatment of the Fine Elements.—Treat with nitric acid until a complete decomposition of the calcareous matter is secured, filter. wash, the residual matter collected upon a filter, and collect the filtrate in a two-liter flask, add a little ammonia, allow to digest, fill the flask with distilled water, leave for 24 hours at repose, and decant:

		Grams.
The decantation furnishes	1st.—A deposit of fine noncalcareous sand weighing dry	3.14
	2nd.—Clayey liquid giving after coagulation by acid filtration, and drying 0.85 grams of clay.	
Then: Total fine elements		5.13
Fine elements determined directly.	Fine noncalcareous sand 3.14 + Clay 0.85	3.99
Fine noncalcareous sand by difference		1.14

Calculating these results to the original quantity of 1,000 grams the following data are obtained:

RESUME.

One thousand grams of dry earth contain:

Pebbles	21 grams.
Gravel	33 "
Organic débris	1 gram.
Fine earth	945 grams.
Total	1000 "

		Grams.		Grams.
945 grams of fine earth contain:	Coarse sand	432	Noncalcareous sand	305
			Calcareous sand	119
			Volatile matter	8
	Fine elements	513	Fine, noncalcareous sand	314
			Clay	85
			Fine calcareous sand	114
			Total	945

As clay are counted all the elements which have remained in suspension in the water after a period of repose of 24 hours. In fact, these elements comprise a notable proportion of very fine sand which is not deposited during that time. In order that the liquid should become entirely freed from this sand it would be necessary to wait several weeks and even several months. Such a prolongation of the analysis is evidently inad-

missible. The period of 24 hours of repose therefore has been adopted. This is merely conventional, in the same way that the period of ten seconds adopted for the precipitation of the gravel is conventional. But this convention is justified by the fact that the substance which is called clay presents, when it has a proper degree of humidity and cohesion, a plasticity entirely analogous to that of natural clay. Moreover, as has already been said, that which is chiefly important in these analyses is the employment of processes always comparable among themselves in their results and generally followed.

233. **The Belgian Method.**—The method of estimating the percentage of sand and clay practiced at the Gembloux Station[63] is essentially that recommended by Schloesing with a few minor modifications.

With the ball of the thumb or with the finger, 100 grams of fine earth are rubbed with water in a porcelain capsule or mortar with a capacity of about 250 cubic centimeters. The suspended particles are poured off with the wash water and the process repeated five or six times, using in all about 200 cubic centimeters of water.

The water containing the sediment is rendered slightly acid (hydrochloric) adding the acid in minute quantities with frequent stirring for about an hour in order to dissolve all the carbonate and to separate the organic acids from the bases with which they are combined.

The liquid is allowed to remain at rest for five or six hours and a part of the liquor decanted to remove any supernatant particles of organic matter which may have passed the sieve in the original preparations of the sample. Filter through a smooth filter about 12 centimeters in diameter, wash until the chlorin has disappeared, and throw the filtrate away.

Break the filter paper over the vessel in which the soil was treated with hydrochloric acid and wash all the contents of the filter into this vessel with as little water as possible (about 100 cubic centimeters at most), add five cubic centimeters of strong ammonia water, allow to stand for three hours, shaking from

[63] Petermann, L'analyse du sol, 15.

time to time and with distilled water make the volume up to 250 cubic centimeters. Stir vigorously with a glass rod, take this out and wash any adhering particles back, leave at rest for 24 hours, and siphon the turbid liquid into a two-liter vessel. Make the volume up again to 250 cubic centimeters and treat as above described and repeat the operation until the water becomes clear. Usually eight or ten washings are necessary. Wash the residual sand into a weighed dish, evaporate to dryness, ignite and weigh. The weight obtained divided by the weight of the original sample gives the per cent of sand. The sand is separated by sieves of varying fineness into coarse, fine, and pulverulent sand.

Add to the ammoniacal liquor collected in the two-liter flask some powdered potassium chlorid (five grams per liter) to hasten the coagulation and rapid deposit of the clay.

After 24 hours siphon the clear liquor, collect the deposited clay in a smaller vessel, allow to remain at rest and decant as much of the clear liquor as possible. Pass through a plain tared filter about nine centimeters in diameter, wash and dry at 150° and weigh the clay.

234. The Italian Method.—Schloesing's method as carried out by the Italian chemists[64] is as follows:

A kilogram of air-dried earth is separated into two portions by a sieve of five millimeter mesh.

With another sieve having spaces of one millimeter, the coarse sand is separated. The pebbles and sand are dried, weighed, treated with hydrochloric acid and again weighed in order to find the quantity of calcareous matter contained in them. In ten grams of the fine earth passing the second sieve the humidity is determined by drying at 100°.

Ten grams are thoroughly mixed in a capsule with from 15 to 20 cubic centimeters of water and after eight to ten seconds the supernatant liquid is poured into a beaker having a capacity of 250 cubic centimeters. The same operation is repeated until there are contained in the beaker the fine sand and the clay, while the coarser sand remains in the capsule.

This last is then dried and weighed and the quantity of calcium

[64] Le stazione sperimentali agrarie Italiane, 1889, 17 : 672 et seq.

carbonate determined by treating it with diluted nitric acid. By means of calcination the organic matter is determined. The liquid decanted in the beaker, the volume of which must not surpass 200 or 250 cubic centimeters, is treated with nitric acid, filtered after some time, washed and the calcium is directly determined by precipitating the solution with ammonium oxalate as will be described further along.

The part in the filter which contains the fine sand, the clay, and the humus material is mixed with water to a volume of about 200 cubic centimeters; there are then added two to three cubic centimeters of ammonia and after two or three hours it is diluted to a liter and strongly agitated.

After 24 hours of rest it is decanted and the residuum is treated a second time with diluted ammonia, decanting after 24 hours. Ordinarily these two treatments suffice, if, however, the earth is very argillaceous, this operation should be repeated three and even four times.

The clay which is found in the liquid suspended in colloidal form coagulates and is precipitated by adding from 30 to 40 cubic centimeters of a saturated solution of potassium chlorid, while the humus substance, under the influence of the ammonia remains dissolved.

Sestini found that the method of Schloesing was the only one which indicated exactly the quantity of clay in the soil. He modified this method by reducing the time of rest from 24 hours, as proposed by Schloesing, to only 12 hours, a reduction which in his opinion does not in the least impair the exactness of the method.

Sestini also proposes 12 treatments instead of six.

235. Method of Williams-Fadejeff.—A very full discussion of the principles of silt analyses and some of the more common methods employed is found in a paper by Williams[65]

In the process finally recommended, *viz.*, the Williams-Fadejeff method, the larger particles are separated after proper pestling and boiling by sieves and the smaller particles passing 0.25 mm. mesh are subjected to separation in water.

[65] Forschungen auf dem Gebiete der Agrikultur-Physik,, 1895, **18** : 225 et seq.

The treatment of this portion is as follows:

The principle on which this method rests is much like that of the beaker process. The apparatus used in this process is composed of glass cylinders of the following dimensions:

a	12	cm.	high	and	6	cm.	in	diameter.
b	12	"	"	"	20	"	"	"
c	12	"	"	"	22	"	"	"
Two *d*	35	"	"	"	17	"	"	"

The soil emulsion previously boiled and having the coarser particles removed by a sieve is placed in a porcelain dish and added little by little to the vessel *a* to a depth of 10 cm., allowed to stand for 5 minutes and the liquid portion poured into *b* and the process continued until the whole sample is in *a* and *b*. The part remaining in *a* is stirred with distilled water, allowed to stand 5 minutes, and poured into *b*, and this is continued until there is no longer any marked turbidity produced.

The cylinder *b*, if not already full, is filled to a depth of 10 cm. with water, its contents well stirred and allowed to stand 24 hours. With a suitable siphon the part in suspension is transferred to one of the cylinders *d*. Water is added to the residue in *b* and this process repeated until the water after 24 hours is no longer turbid.

To each of the *d* cylinders is added 10 cc. of a concentrated calcium chlorid solution and the contents stirred until the suspended silt is coagulated. When the supernatant liquid is clear it is drawn off by a siphon. The precipitate in the two *d* cylinders is removed for later investigation. The soil precipitate remaining in *b* is boiled for 42 hours, adding water from time to time in a porcelain dish covered with a watch glass, passed through a sieve of 0.25 mm. mesh again into *b* and water added to the depth of 10 cm. The lost portion of the water used for filling up to that depth should be got from renewed washings of the residue in cylinder *a*.

The contents of *b* are well shaken and allowed to rest for six hours and the liquid part siphoned into *c*. The muddy water in *c* is allowed to stand for 24 hours and then siphoned into *d*, and this process is continued until the water is clear. The wash waters added to that previously collected from the subsidence in

d are again treated with the concentrated chlorid of calcium solution, the solution after the subsidence of the silt removed by a siphon and the collected silt dried and weighed. This process is justly regarded as very tedious and appears to have no superiority in any respect to the beaker method. For further details of the process which are given at great length the reader is referred to the original article.

236. Comparison of the Above Methods with Others.—Puchner has compared the results obtained by the above method with those given by the Hilgard, Kühn and Mayer's processes.[66]

The data secured are found in the following table:

Kind of soil.	Clay Hilgard. Per cent.	Schlamm Fadejeff-Williams. Per cent.	After Kühn.	After Mayer.
Porcelain earth	43.28	44.44	100.00	100.00
Sandy soil.....	10.40	19.90	59.46	60.40
Quarz sand.....	0.50	1.58	9.00	10.90

Puchner asserts that the data obtained by the Fadejeff-Williams method are less likely to be burdened with error than those secured by the Hilgard process. His reasoning, however, based as it is on such a small number of analyses, is far from convincing. The serious manipulatory objections to the use of the Fadejeff-Williams method are sufficient to render the process only of scientific and not practical interest.

237. Apparatus of Gawabowski.—This apparatus and method are based largely on the principle of the process of Nöbel and are intended more for commercial and farmers' use than for scientific purposes.[67] The author also recommends its use in the separation of Thomas slag. Its cheapness and ease of use recommended it for the purpose above named. The author compared the results obtained with those given by Nöbel's apparatus and found them quite concordant.

238. Fine Sands in a Soil Rich in Humus.—Schloesing has prepared a method for automatically separating the fine particles just above the colloidal particles of a soil, rich in humus (*terre*

[66] Die landwirtschaftlichen Versuchs-Stationen, 1901–02, **56** : 145.

[67] Zeitschrift für analytische Chemie, 1901, **40** : 776.

vegetale) by the rate at which they pass through the center of a mass of water and by the weight of particles passing in a given time.[68]

A cylindrical vessel 33 centimeters long having a bottle shape neck at each end is so arranged that by an ingenious device in connection with a mariotte bottle a certain quantity of water carrying the fine particles is delivered at the lower orifice and collected in a series of capsules moved by clock-work. The mariotte bottle and the clock-work permit the analyst to leave the apparatus to automatic working, after it is once started. The operator who spends one hour and 20 minutes in starting the process in the afternoon will find the analysis complete the morning of the morrow. For the details of construction of the apparatus and of the manipulation the reader is referred to the original paper.

239. **Method of Nefedof.**—This method is based upon the theoretical assumption that particles of a given density and size, evenly distributed through a liquid (water), obey the same laws of descent as if falling in the same medium in independent particles. A necessary condition for the conduct of the method is that the mixture do not exceed a certain density, otherwise a flocculation of the particles will take place, and the independence of the individual particles be lost. To avoid this the author recommends a trituration of the moist soil with a soft pestle until all flocculations are destroyed and the subsequent suspension of the mass in water for a given time. The difficulties of securing in practice the theoretical conditions prescribed are too great to justify a hope of great improvement as a result of the method.[69]

SEPARATION OF THE SOIL PARTICLES BY A LIQUID IN MOTION.

240. **General Principles.**—The laws, already discussed, applying to the subsidence of a solid particle in a liquid, are equally applicable to the separation of the particle by imparting an upward motion to the liquid at a given rate. If a solid particle subside in a given liquid at the rate of one millimeter per second it follows that this particle will remain at rest if the liquid be set in motion

[68] Comptes rendus, 1903, **137** : 369.

[69] Journal (Russian) für experimentelle Landwirtschaft, 1902, 447.

upward with a like velocity. If the velocity be greater the particle will be carried upward and eventually out of the containing vessel. Such a particle is said to have a hydraulic value of one millimeter per second. If there be a perfect separation of a soil into its constituent particles and no subsequent flocculation, all the particles of one millimeter hydraulic value and less will be separated by a current of the velocity mentioned.

The general principles on which the separation rests, therefore, are the securing of the proper granulation of the sample and the maintenance of a fixed velocity of the current until the separation is finished. The separation must be commenced with a period of subsidence so as to remove first of all the suspended clay or impalpable particles. The velocity can then be increased in a certain fixed ratio to secure a separation into particles of any required hydraulic value.

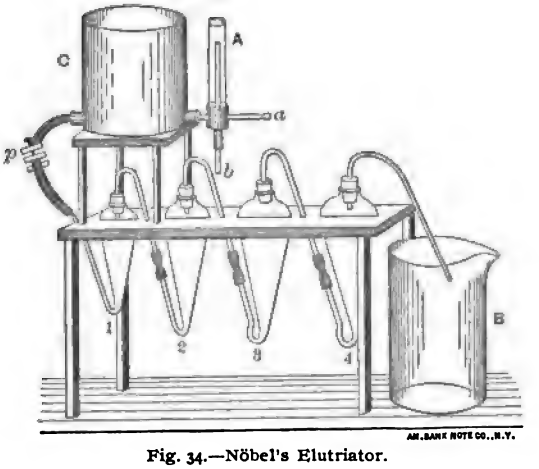


Fig. 34.—Nöbel's Elutriator.

241. Noebel's Apparatus.—One of the earliest methods of separating the soil particles by a moving liquid is that of Nöbel.[70] The apparatus is shown in Fig. 34. The four separating vessels 1, 2, 3, 4 are of glass, pear-shaped, and have a relative capacity of 1^3, 2^3, 3^3, 4^3, or 1 :8 :27 :64. No. 4 has an outlet tube leading to the beaker B, of such a capacity as to allow the passage of just nine

[70] Zeitschrift für analytische Chemie, 1864, **3** : 89.

liters of water in 40 minutes, constant pressure being maintained by means of a Mariotte's bottle or of the constant level apparatus A, *a, b,* which is connected with the main water supply through the tube *a* by means of a rubber hose. The reservoir C should hold about ten liters. The sample of soil to be separated should be previously boiled and passed through a sieve having circular openings one millimeter in diameter. The flask in which the sample is boiled is allowed to stand for some time when the muddy supernatant liquid is poured into elutriator No. 2 and the remaining sediment washed into No. 1. No. 1 is filled with water by connecting it with the water supply and opening the pinch-cock *p*. The water is carefully admitted until the air is all driven out and Nos. 1 and 2 connected. The cock *p* is then opened and the vessels all filled, and the water allowed to run into B for forty minutes, the level being maintained uniformly at A.

Of the water used, 4 liters are found in the elutriating vessels and 5 liters in the receiving vessel No. 5. The apparatus is left standing for an hour until the liquid in the elutriators is clear and the portions in each vessel are received on weighed filters dried at 125°, and the weight of each portion determined.

It is recommended that the loss on ignition of each part be also determined. The separated particles thus secured are classified as follows:

No. 1. Débris and gravel. No. 2. Coarse sand. No. 3. Fine sand. No. 4. Clayey sand. No. 5. Finest parts or clay.

Although the method of Nöbel has been much used, the results which it gives are entirely misleading. The convection currents produced in the conical vessels by the passing water and the flocculation of the soil particles prevent any sharp separation into classes of distinct hydraulic value. The process may be useful for a qualitative test, but its chief claim to a place in this manual is in its historic interest arising from its use in the first attempts at silt analysis.

242. Method of Dietrich.[71]—The difficulties attending the silt separation by the Nöbel method, led Dietrich to construct an apparatus in which the sides of the elutriating vessels are parallel,

[71] Zeitschrift für analytische Chemie, 1866, **5** : 295.

but these vessels, with the exception of the first, are not set in an upright position.

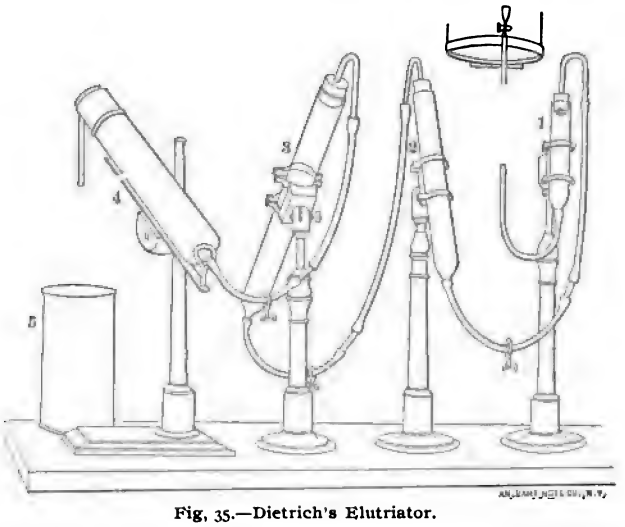


Fig. 35.—Dietrich's Elutriator.

The apparatus (Fig. 35) consists of a series of cylindrical vessels connected by rubber tubing.

The elutriators are of the following dimensions:

No. 1. Seventeen centimeters long, 2.8 centimeters in diameter, position upright.

No. 2. Thirty-four centimeters long, four centimeters in diameter, inclined 67°.5.

No. 3. Fifty-one centimeters long, 5.2 centimeters in diameter, inclined 45°.

No. 4. Sixty-eight centimeters long, 6.4 centimeters in diameter, inclined 22°.5.

The rubber tubes passing from one vessel to the other are furnished with pinch-cocks so that each one of the elutriating vessels can be shut off from the others and independently removed from the circuit.

The stream of water is made to pass through the apparatus under a constant pressure of one meter.

Only the fine earth, boiled with water or hydrochloric acid, is to be placed in the apparatus. The part coming through a sieve with a mesh 0.67 millimeter is to be used and placed in No. 1. About

30 grams of soil are employed for each elutriation. Before adding the soil, the air is completely removed from all parts of the apparatus by connecting it with the water supply and allowing it to be filled with water.

The rate of flow is controlled by the orifice of the last effluent tube and the analyst is directed to continue the operation until the effluent water collected in the beaker glass (5) is clear. The particles then remaining in each of the vessels are collected separately.

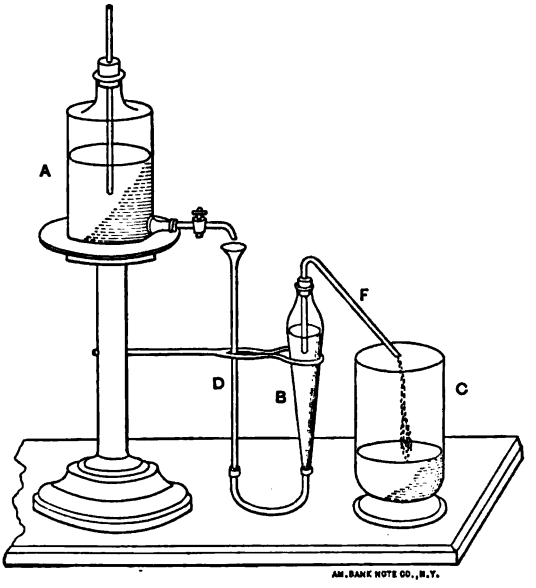


Fig. 36.—Masure's Silt Apparatus.

The author of the method claims that in respect of likeness of particles the results are especially gratifying and that duplicate analyses give results fully comparable. The process, however, has not commended itself to analysts, but it marks a distinct progress toward the principles of later investigators. Had each of the elutriating vessels been placed upright and the rate of flow determined, the apparatus of Dietrich would have served, to a certain extent, for the more rigid investigations of his successors.

243. **Method of Masure.**[72]—From 10 to 15 grams of the sift-

[72] Encylopédie chimique, **4** : 137.

ed earth is carefully mixed with 200 cubic centimeters of water. It is then introduced into a doubly conical elutriator B, Fig, 36, of about 250 cubic centimeters capacity. A current of distilled water is allowed to flow from a mariotte bottle A, which secures a regular and constant flow. The bottle A is joined to the elutriator B by means of a rubber tube and the vertical glass tube D, the top of which is expanded into a funnel for the purpose of receiving the water from the mariotte flask. The current of water flowing upward through the elutriator B carries in suspension the most finely divided particles of clay, and these are collected with the emergent water in the receiver C. The sand and coarser particles of clay remain in the elutriator. The water flows out by the tube F, the diameter of which should be less than that of D. When the emergent water becomes limpid the operation is terminated. After the apparatus is disconnected, the water is decanted from the sand in the elutriator, and the whole residue is weighed after drying for two hours at 110°.

The fine soil collected in C may also be separated and weighed, for control, after drying as above.

The pebbles and coarse sand separated by the sieves should also be weighed. By this process the soil is separated into four portions; *viz.*,

(1) Pebbles. (2) Coarse sand. (3) Fine sand and other materials not carried off by the current of water. (4) Fine soil, carried into the receiver C.

244. Method of Schoene.—The method of Schöne[78] is based on the combination of a cylindrical and conical separatory tube through which the flow of water is regulated by a piëzometer.

If, in the process of silt separation, the water move perpendicularly upward with a given velocity, *e.g.* = v the separation is dependent:

(1) On the volume of the silt particles, (2) on their specific gravity, and, (3) on their state of disintegration.

If it be assumed that the silt particle is a sphere with a diam-

[78] Ueber Schlämmanalyse, Bulletin de la Societe imperiale des naturalistes de Moscow, 1867, **40**, First part, 324.
Zeitschrift für analytische Chemie, 1868, **7** : 29.

eter = d, then according to Newton's law of gravity, the following formula would be applied:

$$d=v^{3}\left(\frac{3Z}{4g\,(S-1)}\right).$$

In the above formula Z = a coefficient which depends on the condition of the surface against which the hydraulic pressure or resistance works, in this case a sphere; g = the acceleration of gravity equivalent to 9.81 meter; and S = the specific gravity of the particle.

Fig. 37.—Schöne's Elutriator.

This expression signifies that in a given case, the velocity of the current in the apparatus is just sufficient to counteract the tendency of a given particle to sink. All particles of a smaller diameter, in such a case, will be carried on by the current, while all of a greater diameter would separate by sedimentation. These theoretical conditions are not met with in practice where silt particles of all shapes and degrees of aggregation abound. These particles, whatever their shape, may be said to have the same hy-

draulic value when carried by the same current. It is necessary, therefore, to secure some uniform standard of expression to assume a normal form of particle and a normal specific gravity. For the form, a sphere is evidently the normal which must be considered and for specific gravity that of quartz is taken; *viz.*, 2.65. The mean coefficient for Z may also be placed at 0.55, although slightly different values are ascribed to it. Substituting these values in the formula, it is reduced to the expression; $d = v^2 \times 0.0000255$ (millimeters). It can, therefore, be said that by this or that velocity of the current, silt particles will be removed of this or that diameter, it being understood that all particles of equal hydraulic value to spherules of quartz of the given diameter are included in each class. In order to have the theoretical formula agree with the results of analysis it is necessary to modify it empirically to read $d = v^{7}/_{11} \times 0.0314$ (millimeter).

This formula is found to agree well with the results obtained for all velocities between 0.1 millimeter and 12 millimeters per second, the ordinary limits of silt separation.

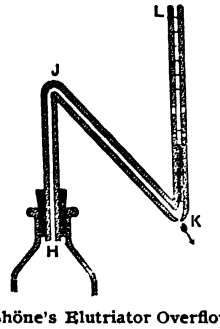


Fig. 38.—Shöne's Elutriator Overflow Tube.

The Apparatus.—The conic-cylindrical elutriating vessel A, B, C, D, E, F, G, Fig. 37, is of glass. The part B, C, is cylindrical, ten centimeters in length and as nearly as possible five centimeters in diameter.

The conical part C, D, is fifty centimeters in length. Its inner diameter at D must not be greater than five centimeters nor smaller than four centimeters.

The bend, D, E, F, should have the same diameter; *viz.*, four to five centimeters.

The part A, B, C, D, and D, E, F, G, may be made of separate parts and joined by a rubber tube.

Outflow Tube and Piëzometer.—The outflow tube and piëzometer, H, J, K, L, are constructed as shown in Fig. 38. Barometer tubing having an internal diameter of about three millimeters is used on the construction of this part of the apparatus. The tube is bent at an angle of 40 to 45 degrees. The knee J must be as acute as possible not to interfere with the inner diameter. The form and especially the magnitude of the outlet are of great importance. It must be circular and nearly 1.5 millimeter in diameter. It must not be larger than 1.67 millimeter nor smaller than 1.5 millimeter. The opening should be so made as to direct the stream of outflowing liquid in the direction shown by the arrow.

The piëzometer L, K, is parallel to the arm H, J, of the delivery tube. Its graduation in centimeters has its zero point in the center of the outlet K. It commences with the one centimeter mark. From one to five centimeters it is divided into millimeters, from five to ten centimeters into one-fourth centimeters, from ten to 50 centimeters into one-half centimeters, and from 50 to 100 centimeters into centimeters. The dimensions given are those required for ordinary soils and for velocities ranging from two-tenths millimeter to four millimeters per second.

For greater velocities, a delivery tube with a larger outlet must be used and the piëzometer must be of greater internal diameter than indicated.

Arrangement of the Apparatus.—The apparatus is conveniently mounted as shown in Fig. 39, giving front and side views of all parts of apparatus in position ready for use. When numerous analyses are to be made much time is saved by having a number of apparatus arranged *en batterie.*

The Sieve.—The soil, before being subjected to elutriation, should be passed through a sieve of which the meshes are 0.2 millimeter square.

The Process.—To measure the diameter of the cylinder, two marks are made with a diamond upon the glass which are distant from each other a certain space, for instance, *h* centimeters. The

space between these two marks is filled with water exactly measured. Suppose that z. cubic centimeters were used, then the diameter D is determined by the fomula:

$$D = \sqrt{\frac{4z}{\pi h}} \text{(centimeters.)}$$

In order to determine that the elutriating cylinder is strictly comparable in all its parts this measurement should be made upon several parts thereof.

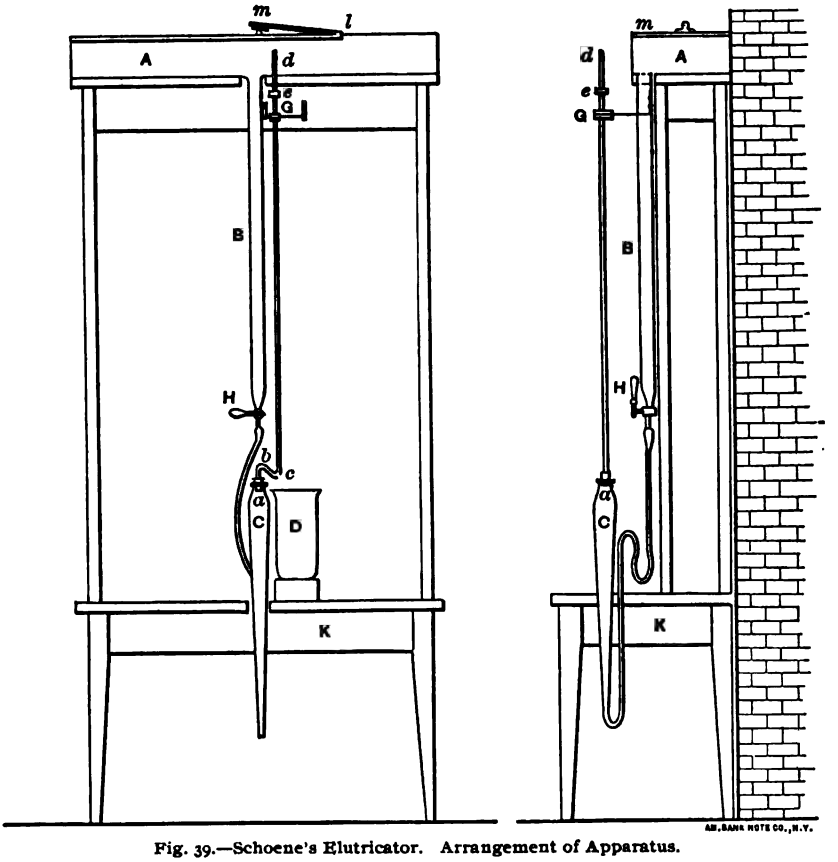


Fig. 39.—Schoene's Elutricator. Arrangement of Apparatus.

The apparatus should now be tested in regard to the quantity of liquid which it will deliver under a given pressure in the piē-

zometer. By means of the stop-cock H the flow of water is so regulated that the outflow at c can be measured at a given height of the water in the piëzometer. Suppose that a cubic centimeters of water flow in t seconds, then the quantity which would flow in one second is determined by the formula, $Q = \frac{a}{t}$ cubic centimeters. Since according to the law of hydraulic outflow the quantities are proportional to the square root of the height of the column it is easy to compute from any given height the quantity which will flow from any other one desired. For the retardation due to capillary attraction, it is sufficient, in general, to take it as a constant quantity; if this constant quantity be represented by C, the observed height of the water in the piëzometer by h, and the quantity of water flowing out by Q, the data required for any given velocity can be calculated from the following proportion:

$$\sqrt{h_1 - C} : \sqrt{h - C} = Q_1 : Q_2.$$

It is necessary to compute the magnitude of this constant C which is to be subtracted. This is accomplished by measuring the quantity of water which flows out at two different heights of the column in the piëzometer. From the foregoing proportion, the value of C is as follows:

$$C = \frac{Q_1^2 h_2 - Q_2^2 h_1}{Q_1^2 - Q_2^2} \text{ (centimeters.)}$$

The value of C can be the more exactly determined as h_1 is greater and h_2 smaller. It is best to choose the lowest height from which an exact reading can be made; that is, by which the regular rise and fall of the level of the water in the piëzometer (in consequence of the formation of drops) just begins to disappear. This usually takes place when $h_2 = 1.5$ centimeters to 1.7 centimeter. For the higher value h_1 it is best to take about 100 centimeters. Suppose, for example, the following results are obtained:

Observed height.		Observed quantity of outflow.		Height of column to be subtracted due to capillary attraction.
h_2 centimeters.	h_1 centimeters.	Q_1 cubic centimeters.	Q_2 cubic centimeters.	C centimeters.
80	1.6	5.53	0.406	1.21
100	1.6	6.13	0.484	1.17
80	1.8	5.53	0.406	1.19
100	1.8	6.13	0.484	1.19

The same quantity of water which flows out in a unit of time passes also at the same time over a cross-section of the elutriating cylinder. The diameter of this cylinder being D the equation is derived

$$v = Q \frac{4}{\pi D^2} \text{ (centimeters.)}$$

Since the velocity in the elutriating cylinder v is directly as the quantity of water overflowing so is

$$v : v_n = \sqrt{h-C} : \sqrt{h_n-C};$$

$$\text{then } v_n = \sqrt{h_n-C}\left(\frac{v}{\sqrt{h-C}}\right)$$

$$\text{and } h_n = v_n^2 \frac{h-C}{v^2} + C. \quad \text{The constant } \frac{h-C}{v^2}$$

is obtained from the means of a number of estimations; for example as illustrated in the following data:

Observed height, centimeters.	Observed quantity of outflow, cubic centimeters.	Corresponding velocity in elutriating cylinder of 4.489 centimeters diameter, millimeters.	Constant. $\frac{h-C}{2}$
1.6	0.406	0.0257	621
1.8	0.484	0.0306	652
80.0	5.530	0.3490	647
100.0	6.130	0.3870	660
		Mean,	645

Then are obtained the following values of h_n and v_n:

$$h_n = 645\ V_n^2 + 1.19 \text{ (centimeters).}$$

$$\text{and } v_n = \sqrt{h_n - 1.19} \times 0.0394 \text{ (centimeters.)}$$

In order to be able easily and rapidly to judge under what pressure the outflow has taken place in any particular instance, a large number of values are computed with the help of the formula given and placed together in tabular form. As an example the following table may serve which was computed for one of the apparatus used. Usually it will be sufficient to test the apparatus for four

different heights and then to interpolate the values for all the others. The numbers marked with a star in the table are those which were determined by experiment; the others were calculated.

Height of column in piëzometer. h cm.	Velocity in the elutriating cylinder of 4.489 cm. diameter. v		Corresponding diameter of silt particles. $d = v^2/_{11}$ 0.0314 mm. mm.
	Observed, mm.	Calculated, mm.	
1.5	0.222	0.220	0.0120
1.6	0.257*	0.252	0.0131
1.7	0.284	0.281	0.0140
1.8	0.306*	0.307	0.0148
1.9	0.323	0.332	0.0155
2.0	0.346	0.355	0.0162
2.5	0.427	0.451	0.0185
3.0	0.531	0.530	0.0210
3.5	0.577	0.599	0.0227
4.0	0.650	0.660	0.0236
4.5	0.694	0.717	0.0254
5.0	0.751	0.769	0.0265
6.0	0.850	0.864	0.0286
7.0	0.942	0.950	0.0304
8.0	1.050	1.028	0.0320
9.0	1.120	1.101	0.0334
10.0	1.170	1.169	0.0347
15.0	1.490	1.460	0.0400
20.0	1.730	1.710	0.0441
25.0	1.940	1.920	0.0476
30.0	2.100	2.110	0.0506
35.0	2.310	2.290	0.0532
40.0	2.460	2.450	0.0556
45.0	2.610	2.610	0.0578
50.0	2.770	2.750	0.0598
60.0	3.030	3.020	0.0635
70.0	3.290	3.270	0.0667
80.0	3.490*	3.500	0.0697
90.0	3.710	3.710	0.0724
100.0	3.870*	3.920	0.0749

Suppose the problem is, by means of the apparatus tested as above to separate into a number of groups a mixture of silt particles, whose hydraulic values are found between the following diameters: 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07 millimeters. The table will show at once under what pressure of water the piëzom-

eter must be placed in order to give the values; *viz.*, 1.4, 2.8, 7.0, 15.0, 29.0, 53.0, and 83.0 centimeters, respectively.

The apparatus described above, is adapted for velocities in the elutriating cylinder varying from two-tenths millimeter to four millimeters per second. The largest silt particles which can be separated by the velocities given above, have approximately a diameter of 0.08 millimeter. For the separation of larger particles a sieve can take the place of the silt apparatus. If, however, it be desired to subject larger particles to silt analysis, the dimensions of the elutriating cylinder and of the outlet of the delivery tube must be changed accordingly.

Preparation of Sample.—The conduct of silt analysis of natural soils must, in certain cases, be preceded by a special treatment of the sample. If the latter be rich in humus the organic substance must previously be separated as completely as possible. With sandy soils this can be accomplished by ignition. With clayey soils, on the contrary, it is to be performed by boiling the soils at least one hour with water which contains from one to two per cent of free alkali. Soils which contain lime must also be subjected to treatment with dilute hydrochloric acid, and the hydrochloric acid must be as carefully removed as possible before the sample is subjected to elutriation; afterward follows the boiling of the sample in the ordinary way with water. This, of course, can be omitted when it has already been treated with boiling dilute alkali. It is also important to remove the larger particles by a sieve before the elutriation begins. It is well to pass a sample through a sieve after it has been boiled, by which all particles of a larger diameter than 0.2 millimeter are removed. This will usually require about one liter of water and this water should be allowed to rest from one to two hours and poured off with the suspended material which it contains. Only what subsides should be brought into the apparatus. In rinsing the sample as much water must be used as will fill the apparatus up to its cylindrical portion.

After the sample has been placed in the apparatus, the water is allowed to enter slowly, being careful to avoid reaching more than the lowest required velocity, until the outflow begins. The water then is so regulated by the stop-cock as to bring it to the desired

height in the piëzometer. This being accomplished, the different velocities which have been decided upon for separating the particles of silt are used one after the other, as soon as all the silt which can be removed at each given velocity, has been secured. From three to five liters of water will be required for the separation of each class of particles. Sometimes the reading of the height of the water in the piëzometer is difficult; as, for instance, when foam or bubbles accumulate therein. These bubbles can be removed by simply blowing into the tube, or dropping into it a little ether. The outflow of water can be received in vessels, beaker glasses, or cylinders, in which it is allowed to subside. The finest particles which remain in suspension in the water are best determined by difference. If it be desired to weigh them directly, the water can be treated with ammonium bicarbonate until it contains from one to two per cent thereof. The precipitation then takes place in a few hours.

The collection and weighing of silt particles are accomplished in the usual way. That which finally remains in the elutriating vessel is taken out after the end of the operation by closing the stop-cock, removing the stoppers with the piëzometer tube, pouring the contents of the elutriating vessel into a beaker glass and rinsing out carefully all adhering particles. Examples of the working of the apparatus follow:

The soil was taken from the Imperial Russian Agricultural Experimental Institute at Gorki. It was a fine clay sand and was carefully treated with hydrochloric acid. The results of the analysis are given in the following table:

Velocities employed in mm.	Largest diameter of the collected particles in mm.	Percentage of silt product obtained in repeated elutriations.		
0.25	0.012	13.4	12.6	11.9
0.5	0.020	9.1	8.7	9.5
1	0.032	21.0	21.4	20.8
2	0.050	30.4	29.8	31.7
3	0.063	16.7	16.1	15.5
4	0.076	5.3	5.5	5.5
	Residue	4.2	4.9	3.8
	Total	100.0	99.0	98.7

Holthof modifies the apparatus of Schöne by putting into the

lower mouth of the elutriator a little mercury so that the particles of earth are deposited upon its surface and are thus better agitated and washed by the current of water.

245. **Mayer's Modification of Schoene's Method.**—An improvement of Schöne's apparatus in the direction of greater simplicity has been tested by Mayer[74] with satisfactory results:

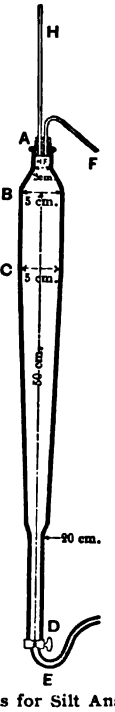


Fig. 40.—Schöne's Apparatus for Silt Analysis, Modified by Mayer.

The apparatus, (Fig. 40), consists of a glass vessel having a glass stop-cock at the bottom for admitting the water. For a distance of 20 centimeters the sides of the tube are parallel and the diameter about one centimeter. Next for a distance of 50 centimeters the tube is conical expanding at a regular rate until the internal diameter reaches five centimeters. For a distance of ten centimeters the vessel is again strictly cylindrical and it is in this cylindrical portion that the separation of the different constituents takes place. The vessel is then rapidly narrowed until

[74] Journal für Landwirtschaft, 1890, **38** : 162.

at the stopper A it is two centimeters in diameter. This stopper carries two glass tubes, one F bent downward to conduct the overflow into the receiving vessels, and one H for the purpose of regulating the rate of overflow by the height of the column of water therein. The orifice of the overflow tube F should be so regulated that with a pressure of five centimeters water in H, one liter shall pass over in ten minutes.

If the separation be conducted in an apparatus thus mounted and graduated with a pressure of two centimeters in H all that portion of the soil which can properly be called clay will pass over. The fine earth, that is, earth in which all coarse particles have been removed by proper sifting, is used in ten-gram lots for each experiment. The residue, after the separation is complete, consists of pure sand or at least pure sand mixed with humus. Before the fine earth is placed in the apparatus, the calcium carbonate therein is removed with hydrochloric acid. The treatment with hydrohloric acid, however, is not to be recommended in soil containing many undecomposed particles of calcium carbonate or dolomite for then large additions to the silt output might be made from these particles, which could not be regarded as coming from the soil as it actually exists. For alluvial soil, however, previous treatment with hydrochloric acid is recommended unconditionally.

246. Schoene's Method as Practiced by Osborne.—The apparatus used by Osborne[75] was obtained from Germany and was similar to that described by Schöne in his original paper, except that it was furnished with a second elutriating tube as suggested by Orth. The modification made by Orth consists, essentially, of a second elutriating tube with straight sides into which the bulk of the soil is introduced, only the final part being carried over into the Schöne's tube proper. Water is supplied to the apparatus under constant pressure by means of a mariotte bottle.

The preliminary treatment recommended by Schöne is omitted, as these steps have been shown to be undesirable, on account of affecting the accuracy of the results.

Twenty grams of the air-dried soil are passed, under water,

[75] Connecticut Agricultural Experiment Station, Annual Report 1887, 145.

through a sieve of one-fourth millimeter mesh. That part of the soil which remains in suspension after being sifted is placed at once in the Schöne tube of the apparatus, the coarser portion being rinsed into the Orth tube. The current is regulated so that the largest particles of quartz carried off have an average diameter of 0.01 millimeter. When all is carried off that can be removed at this rate the current is increased until the largest quartz grains passing off have a diameter of 0.05 millimeter.

As noticed by Hilgard with Schulze's apparatus, secondary currents are formed during the process of elutriation which descend along the walls of the conical portion of the Schöne's tube and some distance along the sides of the cylindrical portion. The tendency of these currents is to produce globular aggregates of particles which fall to the bottom. They are broken up from time to time by increasing the velocity of the current but even this method fails to disintegrate a considerable quantity of them.

247. Statement of Results.—Two samples of soil from the garden of the experiment station analyzed by Schöne's method gave the following proportions of sediment.

In the table the term clay is used to designate all that part of the soil which has diameters less than 0.01 millimeter and which remains suspended after 24 hours standing in water having a depth of 200 millimeters.

SOIL FROM GARDEN OF THE EXPERIMENT STATION.—NOT BOILED.

	A.	*B.*	*C.*
Above 0.25 millimeter	48.82	48.82	48.82
0.25–0.05 millimeter	27.36	29.94	22.37
0.05–0.01 "	8.63	6.07	13.70
0.01 " and less	7.36	7.31	7.20
Clay (by difference)	1.00	1.03	1.08
Loss on ignition	6.83	6.83	6.83
	100.00	100.00	100.00

The column *A* contains the results of the Schöne-Orth method, *B* contains the results of *A* corrected by the beaker method, and *C* represents the average of three direct beaker elutriations according to the method of Osborne.

The differences which these figures show are found to be due to imperfect separation of the finer grades from the coarser and

even when the various fractions separated by the Schöne method are subjected to beaker elutriation and the portions separated from them added to the grades to which they properly belong the Schöne elutriator was found to effect far less exact separations than the beaker method.

Samples of prairie soil from Mercer County, Ill., not boiled, were examined by the two methods with the following results:

	Schöne-Orth elutriation.	Beaker method.
Above 0.25 millimeter	0.76	0.62
0.25–0.05 millimeter	11.25	2.42
0.05–0.01 "	52.65	43.58
0.01 "	14.84	31.58
Clay	4.44	5 81
Loss on ignition	14.49	14.49
	98.43	98.50

In this case it is seen that Schöne's method varies considerably from the beaker method and if the beaker method be regarded as correct the Schöne method is evidently less reliable.

In the next table are given the data of the examination of brick clay from North Haven, Conn., by the two methods.

BRICK CLAY FROM NORTH HAVEN, CONN.

	Shöne-Orth elutriation.	Beaker method.
Above 0.25 millimeter	1.02	1.02
0.25–0.05 millimeter	3.91	0.76
0.05–0.01 "	29.63	20.95
0.01 " and less	58.58	71.01
Loss on ignition	6.60	6.60
	99.74	100.34

The failure of the Schöne method to give the results obtained by the beaker method is ascribed to the fact that it is impossible for the current of the strength used to disintegrate the clay and further that the particles after they are once separated tend to coalesce by the currents produced by the elutriating process.

248. The Berlin-Schoene Method.—Osborne has also made a study of the Schöne method as modified by the soil laboratory of Berlin. The directions for the analysis by this laboratory method are as follows:

Five hundred grams of the soil are sifted through a sieve with circular holes two millimeters in diameter. Of the earth passing the sieve from 30 to 100 grams are boiled in water with constant

stirring from one-half to one hour or longer, according to the character of the soil. The finer the texture of the soil the smaller the quantity taken and the longer the time of boiling. Treatment with acids or alkalies is not practiced.

The finer portion of the soil remaining suspended in the water, after boiling, is poured into the Schöne tube, the remaining coarse part is rinsed into the Orth tube. The clay, together with the finest sand, is collected in a separate vessel, the water in which it is suspended is evaporated and the residue after drying in the air is weighed. The rest of the operation is carried out as previously described except that the products of elutriation are not ignited but weighed air-dried, in order that they may be further examined, chemically if desired. By proceeding in this manner the following results were obtained:

SOIL FROM GARDEN OF THE EXPERIMENT STATION, BOILED FORTY-FIVE MINUTES.

Separations by the Berlin-Schöne method.

	Air-dried.	Ignited.
Above 0.05 millimeter	72.63	71.76
0.05–0.01 millimeter	14.17	12.53
0.01 " and less	12.97	9.38
Loss on ignition	....	6.83
	99.77	99.50

For the sake of comparing the mechanical separation attainable by this procedure with those yielded by other methods, the air-dried products were ignited and again weighed and examined.

By subtrating from the ignited portion above 0.05 millimeter, 49.37 per cent, the amount of this soil that remained on a 0.25 millimeter sieve, the fraction between 0.25 millimeter and 0.05 millimeter is found, and the separations in this analysis may be compared with those previously obtained by the beaker method as follows:

SOIL FROM GARDEN OF EXPERIMENT STATION.

		Beaker method.		
	Berlin-Schöne, boiled forty-five minutes.	Boiled twenty-three hours average of four analyses.	Pestled not boiled.	Not boiled nor pestled, average of three analyses.
Above 0.25 millimeter	49.37	47.77	48.82	48.82
0.25–0.05 millimeter	21.39	20.75	22.44	22.37
0.05–0.01 "	12.53	11.18	12.55	13.70
0.01 clay included	9.38	13.47	9.36	8.28
Loss on ignition	6.83	6.83	6.83	6.83
	99.50	100.00	100.00	100.00

Osborne concludes from the above facts that the Berlin-Schöne method, while showing close agreement with the beaker method, does not give results which are identical with that method. On subjecting portions separated by the Berlin-Schöne method to the beaker analysis additional separations were secured. In the case of heavy loams the inability of the Berlin-Schöne method to effect even a rough or approximate separation of the several grades becomes very conspicuous.

The latest form and methods of manipulations for the process vary but little from the foregoing details.[76]

This method has been in use in the Royal Prussian Geological Survey for 25 years and is highly recommended as reliable and satisfactory.

249. Method of Hilgard.—Two important principles lie at the foundation of this method; *viz.*, 1, the use only of separating vessels of true cylindrical shape and 2, the employment of a mechanical stirrer to break up the floccules formed during the process of separation. The points in the apparatus to be considered are uniformity of the cross-section of the elutriator at every point, exact perpendicularity of position, careful control of the rate of flow and continuous operation of the mechanical stirrer. According to Hilgard's observations the stirring due to the current of water alone is not sufficient to break up the floccules unavoidably formed during the separation, while any inclination of the sides of the elutriating vessel from the perpendicular due either to a conical shape or false position favors in the highest degree the formation of floccules due to reflex currents formed in the body of the liquid.

In order to carry out the idea suggested by Türschmidt of substituting for the accidental and indefinite products usually appearing in the statements of silt analyses sediments of known and definite hydraulic value a constant head of water is used, secured by means of a mariotte bottle connecting with the tube delivering the current through a cock provided with an arm moving on a graduated arc.

According to Hilgard the separation of sediments by the meth-

[76] Wahnschaffe, Wissenschaftliche Bodenuntersuchung, Second edition 31 and 40.

od of subsidence does not possess the analytical accuracy of the moving liquid method, especially when the latter is combined with mechanical stirring. The subsidence method requires close and continuous attention and in the case of fine sediments tending to flocculation the difficulties of the method are greatly increased. The views of Hilgard in respect of the laboriousness of the subsidence method lose, however, some of their force since the modifications of Osborne have come into use. The simplicity and cheapness of the apparatus required for subsidence give it at the start many advantages over the more elaborate process with a churn elutriator. For rigid scientific investigation, however, the method of Hilgard is commended as a standard of comparison in all cases.

There is one important point in which the separation of the silt particles by translation with water has a great advantage over any method of sedimentation; *viz.*, in the former the particle to be freed and separated is carried in a direction where it meets constantly, decreasing numbers of particles and thus the tendency to collide and coalesce is constantly weakened.

250. The Elutriator.—The instrument devised by Hilgard[77] for the purpose of breaking up these flocculent aggregates is shown in Fig. 41, and a simpler form of Schöne's elutriator, in Fig. 42, which can serve for grain sizes above eight millimeters hydraulic value. The latter is conveniently selected so as to have half the cross-section of the former, so that with the same position of the index lever the velocity will be just doubled. The cylindrical glass tube, 2 Fig. 41, of about forty-five millimeters inside diameter at its mouth, and 290 to 300 millimeters high, has attached to its base a rotary churn consisting of a brass cup, shaped like an egg with point down, so as to slope rather steeply at base, and thrice perforated; *viz.*, at the bottom for connection with the relay reservoir, and at the sides for the passage of a horizontal axis bearing four grated wings. This axis, of course, passes through

[77] Bulletin 38, Bureau of Chemistry, Department of Agriculture, 60.
Proceedings American Association for the Advancement of Science, Portland (22nd) meeting, 1873, 54 et seq.
Proceedings of the 8th Annual Meeting of the Society for the Pro motion of Agricultural Science, 1887, 48 et seq.

stuffing boxes, provided with good thick leather washers, saturated with mutton tallow. These washers, if the axis runs true, will bear a million or more revolutions without material leakage. When a leakage is noted additional washers may be slipped on without emptying the instrument, until the analysis is finished. For the finest sediments, from five to six hundred revolutions per minute is a proper velocity, which may be secured by clock work, turbine or electric power. The driving pulley should not be directly connected with the axis, both because it is liable to cause leakage, and because it is necessary to be able to handle the

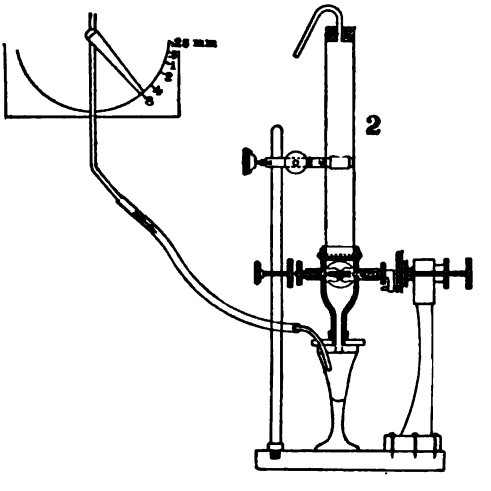


Fig. 41.—Hilgard's Churn Elutriator.

elutriator quickly and independently. The indirect connection is accomplished by the use of "dogs" on the pulley and churn axis. For the grain size of one to eight millimeters hydraulic value lower velocities are sufficient; too low a velocity causes an indefinite duration of the operation and may be recognized by the increase of turbidity as the velocity is increased.

As the whirling agitation caused by the rotation of the dasher would gradually communicate itself to the whole column of water and cause irregularities, a wire screen of 0.8 millimeter aperture is cemented to the lower base of the cylinder.

The relay vessel should be a thick, conical test glass with foot; its object is to serve as a reservoir for the heavy sediments not concerned at the velocity used in the elutriator tube, and whose presence in the latter or in its base, the churn, would cause abrasion of the grains and changes of current velocity such as occur in the apparatus of Schöne. It is connected above with the churn by a brass tube about ten millimeters in clear diameter, so as to facilitate the descent of the superfluous sediments, which the operator, knowing the proportion of area between the connecting tube and elutriator, can carry to any desired extent; thus avoiding the disturbance of the gauged current velocities, as well as all material abrasion.

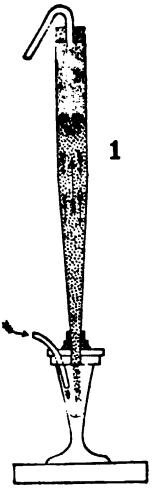


Fig. 42.—Improved Schoene's Apparatus with Relay.

A glass delivery tube should extend quite half way down the sides of the relay vessel, to insure a full stirring up of the coarse sediments when required. By means of a rubber hose, not less than 20 inches in length, this delivery tube connects with the siphon carrying the water from near the bottom of the mariotte bottle, conveniently made of a ten-gallon acid carboy. A stopcock provided with a long, stiff index lever, moving on an empirically graduated arc, regulates the delivery of water through the siphon. Knowing the area of the cross-section of the elutriator tube, the number of cubic centimeters of water which should

pass through it in one minute, at one millimeter velocity, is easily calculated, and from this the lever positions corresponding to other velocities are quickly determined and marked on the graduated arc. The receiving bottle for the sediments must be wide and tall, so as to allow the sediment to settle while the water flows from the top into the waste pipe.

Thus arranged, the instrument works very satisfactorily, and by its aid soils and clays may readily be separated into sediments of any hydraulic value desired. But in order to insure correct and concordant results, it is necessary to observe some precautions; *viz.*,

(1) The tube of the instrument must be as nearly cylindrical as possible and must be placed and maintained in a truly vertical position. A very slight variation from the vertical at once causes the formation of return currents, and hence of molecular aggregates on the lower side.

(2) Sunshine, or the proximity of any other source of heat, must be carefully excluded. The currents formed when the instrument is exposed to sunshine will vitiate the results.

(3) The mariotte bottle should be frequently cleansed, and the water used be as free from foreign matters as possible. For ordinary purposes it is scarcely necessary to use distilled water. The quantities used are so large as to render it difficult to maintain an adequate supply, and the errors resulting from the use of any water fit for drinking purposes are too slight to be perceptible, so long as no considerable development of the animal and vegetable growths is allowed. Water containing the slimy filaments of fungoid growths and moss prothalia, algæ, vorticellæ, etc., will not only cause errors by obstructing the stop-cock at low velocities, but these organisms will cause a coalescence of sediments that defies any ordinary churning, and completely vitiates the operation.

(4) The amount of sediment discharged at any time must not exceed that producing a moderate turbidity. Whenever the discharge becomes so copious as to render the moving column opaque, the sediments assume a mixed character, coarse grains being, apparently, upborne by the multitude of light ones whose hydraulic value lies considerably below the velocity used, while

the churner also fails to resolve the molecular aggregates which must be perpetually reforming where contact is so close and frequent. This difficulty is especially apt to occur when too large a quantity of material has been used for analysis, or when one sediment constitutes an unusually large portion of it. Within certain limits the smaller the quantity employed the more concordant are the results. Between ten and fifteen grams is the proper amount for an instrument of the dimensions given above.

251. Preparation of the Sample.—In some cases simple sifting will be sufficient to prepare the air-dried soil for the elutriator. In most cases, however, some mechanical aid must be invoked to secure particles of sufficient fineness. Nothing harder than a rubber pestle should be used and care must be taken not to break up any calcareous or ferruginous masses which the particles of fine soil may contain. The use of water in this mechanical attrition should be avoided, if possible, but in some heavy clay and adobe soils wetting becomes necessary. In this case the parts separated by the sieve are collected separately and the turbid mass removed by water and dried for further examination.

A sieve of 0.5 millimeter mesh is recommended as the best because that is almost exactly the diameter of the particles passing off at the maximum velocity of 64 millimeters per second to which the elutriator is adapted. The particles passing the 0.5 millimeter mesh are called fine earth.

252. Preparation by Boiling.—The method of preparation by boiling may be applied to all samples of fine earth. The fact pointed out by Osborne, that the diffusibility of some clays is diminished by long boiling, renders it important to restrict the time of this operation as much as possible. With most soils from eight to 15 hours will be long enough, occasionally extending to even 24 hours. A thin long-neck flask of about one-liter capacity should be used; filled three-quarters full with distilled water and the sample of soil added. The flask is supported over the lamp on a piece of wire gauze at an angle of 45°. It carries a cork with a long condensing tube. At first the boiling goes on smoothly, but after a time violent bumping may supervene, endangering the flask but promoting the object in view.

The contents of the flask are transferred to a beaker and diluted with distilled water to one and a half liters, shaken and allowed to settle for a time necessary to allow all particles of 0.25 millimeter hydraulic value to reach the bottom. The supernatant turbid liquid is decanted and the process repeated with smaller quantities of water until no further turbidity is produced. The united waters, of which there will be from four to eight liters, are well shaken and a proper time allowed for the 0.25 millimeter hydraulic value sediments to fall. This last step is necessary to remove any such sediments which may have been carried over mechanically in the first separation. The dilution being very great, a fairly perfect separation is thus secured and the sediments are then ready for the elutriator.

253. **Separation of Clay and Fine Silt.**—The property which pure clay possesses, of remaining suspended almost indefinitely in pure water, affords a ready means of separation from the silt particles of less than 0.25 millimeter hydraulic value. But the finest silt particles subside so slowly that this method of separation is too long to become practically applicable to secure a perfect demarcation between the finest silt and so-called colloidal clay.

Hilgard recommends the following procedure: The clay water from the previous separation is placed in a cylindrical vessel of such a diameter as to allow the column of water to be 200 millimeters high where it is allowed to settle for 24 hours. When the clay is very abundant a longer time may be allowed; *viz.*, from 40 to 60 hours. The line of separation between the dark silt below and the translucent clay above is sharply defined. Finally the clay water is decanted and the remaining liquid poured off leaving the sediment as sharply defined as possible. The sediment is rubbed with a rubber pestle and a few drops of ammonia water added. Distilled water is added, the beaker well shaken or stirred to break up the floccules that may have formed and subsidence permitted as before. This operation is repeated from six to nine times until the water remains quite clear after subsidence or the decanted turbid water fails to be precipitated by brine showing the suspended matter to be fine silt and not clay.

The diameter of the particles of silt thus obtained is from 0.001 to 0.02 millimeter, and is is impossible to obtain it quite free from any admixture with clay.

254. Estimation of the Colloidal Clay.—The importance of the colloidal constituent of the clay is such as to make its direct determination desirable. The volume of the clay waters at this stage of the analysis may amount to 20 liters. One method of determination consists in evaporating an aliquot portion and this method will yield good results if the sample be free from soluble salts and the quantity taken be not too small. At least 500 cubic centimeters should be used for this purpose. A better method consists in precipitating the clay by means of a saline solution. A saturated solution of salt is recommended for this purpose of which 50 cubic centimters are sufficient to precipitate the clay from one liter of the clay water. The precipitation is hastened by heating. Each portion of the clay water should be precipitated as soon as obtained, the total volume of the precipitate at the end of 24 hours is thus reduced to a minimum. The clay water from the succeeding separations of the same analysis can be mixed with the precipitate which diffuses therein, thus promoting the precipitation of the rest of the clay inasmuch as the separation takes place more readily where more clay is present. When all the clay is thus collected it can be gathered on a tared filter and washed with weak brine. Pure water may not be used because of the diffusibility of clay therein. After drying at 100° and weighing it is washed with a weak solution of ammonium chlorid until all sodium is removed. The filtrate is evaporated to dryness, ignited at low redness, and weighed. The weight of the sodium chloride thus obtained plus the weight of the filter deducted from the total weight gives the weight of the clay precipitate. Whenever the clay collected as above will not diffuse in water it may be washed with water and its weight directly obtained. An excess of iron in clay will usually allow of the above treatment.

255. Properties of Pure Clay.—The percentage of pure clay as obtained by the procedure described is about 75 in the finest natural clays, 45 in heavy clay soils, and 15 in ordinary loamy soils.

When freshly precipitated by brine it is gelatinous resembling a mixed precipitate of iron and aluminum oxids. Its volume greatly contracts on drying, clinging tenaciously to the filter, from which it may be freed by moistening. On drying, it becomes hard, infriable, and often resonant. It usually possesses a dark brown tint due to iron oxid. Under the action of water it swells up like glue, the more slowly as the percentage of iron is greater. In the dry state it adheres to the tongue with great tenacity. The particles composing this colloidal clay remaining in suspension as described are extremely minute. With a magnifying power of 350 diameters Hilgard states that no particles can be discerned.

256. Chemical Nature of the Fine Clay.—The fine particles separated as above consist essentially of hydrous aluminum silicate or kaolinite. It doubtless contains, however, other colloids or hydrogels whose absorptive powers are similar to those of clay. It appears also to contain sometimes free aluminum hydroxid, and colloidal ferric hydroxid, and amorphous zeolitic compounds.

While the most careful mechanical separation can give at best only approximately the really plastic kaolinite substance, yet it is far closer than that attained by determination of total alumina with boiling sulfuric acid. By the latter treatment all the lime-kaolinite particles are decomposed and the method does not lead to even an approximate estimate of the soil's plasticity.

257. Separation of the Fine Sediments.—The sediments remaining after the separation of the clay and fine silt are ready for separation in the churn elutriator. The apparatus mounted, as already described, is brought into use by beginning with a low velocity of the water in the upright tube. The rate of flow should be set at from 0.25 millimeter to 0.50 millimeter per second, and the churn put in motion.

When the elutriating tube is partly full of water the sediments should be poured in from a small beaker which is perfectly cleaned by means of a washing flask. The stopper and delivery tube of the elutriator are then put in place. The rate of flow should be so regulated that the sediments shall have had a few seconds of

subsidence before the water is within thirty millimeters of the top. At this point the required velocity for the first sedimentation should be turned on; *viz.*, 0.25 millimeter per second. At first the sediment passes off rapidly and the water in the elutriator is distinctly turbid. This excess of turbidity ceases in a few hours and then some attention is necessary in order to determine when the process is complete. In fact it never is completely finished, but where no more than one milligram of silt comes off with one liter of water it may be said to be practically done. The time required for the first operation varies from 15 to 90 hours. Downward currents in the elutriator are likely to form in spite of all precautions, and floccules of silt adhere to its walls. These should be detached from time to time with a feather in order to bring them again in contact with the churn.

Hilgard has found that, practically, 0.25 millimeter per second is about the lowest velocity available within reasonable limits of time, and that by successively doubling the velocities up to 64 millimeters a desirable ascending series of sediments is obtained; provided always, that a proper previous preparation has been given to the soil or clay. It would seem that according to the prescription given above for the preliminary sedimentation, no sediment corresponding to 0.25 millimeter velocity should remain with the coarser portion. That such is nevertheless always the case, often to a large percentage, emphasizes the difficulty, or rather impossibility, of entirely preventing or dissolving the coalescence of these fine grain sizes by hand stirring, as in beaker elutriation. It is only by such energetic motion as is above prescribed that this can be fully accomplished, and the delivery of 0.25 and 0.50 millimeter hydraulic value really exhausted.

It is desirable to run off the upper third of the column at intervals of from 15 to 20 minutes by temporarily increasing the velocity. Recent sediments, river alluvium, etc., are more easily separated than soils of more ancient formation. The second, third, etc., separations are naturally accomplished in much less time than the first. The respective velocities of the separations should be 0.25 millimeter, 0.50 millimeter, one millimeter, two millimeters, four millimeters, eight millimeters, 16 millimeters, 32

millimeters, and 64 millimeters a second. Below a velocity of four millimeters a second the mechanical stirrer is indispensable. Above this velocity the current of water in the conical base will be sufficient to bring the desired particles into the ascending column. At this velocity also a smaller elutriating tube having one-half or one-quarter the cross-section of the first may be employed to hasten the operation and diminish the quantity of water required. The quantity of water required for a complete separation is from 100 to 120 liters. Any soft water free of organic matter may be used, but distilled water is best. Hard water should be avoided.

The mean time required for the different separations is as follows: 0.25 millimeter hydraulic value, 35 hours; 0.50 millimeter hydraulic value, 20 hours; one millimeter hydraulic value, seven and a half hours; two to sixty-four millimeters hydraulic value, eight hours. With proper arrangements for night work, an analysis may be finished in three or four days not counting the time required for the previous separation of the clay.

258. Weighing the Sediments.—The sediments should be dried at the same temperature used for drying the soils. Hilgard dries both at 100°. Great care should be used in weighing the exceedingly hygroscopic clay sediments. In the case of the sediment of 0.25 millimeter hydraulic value it is allowed to subside as much as possible and after removing the supernatant water the residue, from 25 to 50 cubic centimeters, is evaporated in a platinum dish and weighed therein. The water can be completely decanted from the other sediments, and they can be dried and weighed without any unusual precautions.

The loss in the separation of clays and subsoils containing but little organic matter is usually from 1.5 to 2 per cent. This loss is partly due to the fine silt which comes off during the whole of the process and which is lost in the decanted waters of the sediments of 0.25 millimeters hydraulic value and above. The procedures indicated above are not strictly applicable to soils rich in humus and other organic matters, but the destruction of these matters by ignition leaves the residual soil in a condition wholly unfit for sedimentary separation.

259. Classification of Results.—A convenient method of stating the results of an analysis may be seen from the following classification. The percentage obtained for each of the classes is to be entered in the column provided for that purpose.

	No.	Names of silt classes.	Diameter of grains in millimeters.	Velocity of current millimeters hydraulic value.	Per cent.
Sieves.	1.	Grits	1 –3	....	2.07
Sieves.	2.	Fine grits	0.5–1	....	
Elutriator without churn.	3.	Coarse sand	0.50	64	0.55
Elutriator without churn.	4.	Medium sand	0.30	32	
Elutriator without churn.	5.	Fine sand	0.16	16	
Elutriator with churn.	6.	Finest sand	0.12	8	0.21
Elutriator with churn.	7.	Coarse silt	0.072	4	1.21
Elutriator with churn.	8.	Large silt	0.047	2	2.92
Elutriator with churn.	9.	Medium silt	0.036	1	7.36
Elutriator with churn.	10.	Silt	0.025	0.5	8.86
Elutriator with churn.	11.	Fine silt separated in elutriator	0.016	0.25	7.85
Beaker sedimentation.	12.	Fine silt separated from clay water	0.010	<0.25	35.22
Beaker sedimentation.	13.	Clay	....	<0.0023	33.16
		Total			99.36

The measurements of diameters in the above table is of the best formed quartz grains in each class. Naturally the actual size of the particles may vary in each class within the extreme limits of the diameter next above and below. It is not easy to indicate in popular language distinctions not popularly made but the grades of particles designated by the names grits, sand and silt, may serve, at least, to establish uniformity of expression. The term grits is thus applied to all grains above one millimeter in diameter up to gravel. Below one millimeter down to 0.1 millimeter may be called sand and below that silt may designate the particles down to an impalpable powder.

260. Influence of Size of Tube.—The diameter of the elutriating tube exerts a sensible influence on the character of the sediments. The friction against the sides of a small tube is comparatively greater than in a large tube. Strictly speaking, no class of sediments strictly corresponds to the hydraulic value calculated from the cross-section of the tube and the quantity of water supplied thereto. The sediments correspond actually to higher velocities, due to the fact that the lateral friction causes a more rapid flow

in the center of the water column. This may be demonstrated by slightly diminishing the velocity while a sediment is copiously discharging. The turbid column then remains stationary while clear water is running off.

261. Statement of Results.—A complete silt analysis of a soil, conducted by the method of Hilgard, depends largely for its practical value on an intelligible tabulation. The method of collating results is illustrated in the table of analyses of Mississippi soils.[78]

The character of the soils entering into the given analyses is as follows:

Nos. 248, 206, 209, 397, 219, belong to the end of the drift period.

No. 230 is one of the two chief varieties of soils occurring in what is known as the flat-woods, a level surface bordering on the cretaceous area, having lower tertiary clays near the surface.

No. 165 is a light soil which occurs in the former in irregular strips and patches, is easily tilled, absorbs rain water readily, but is subject to drought and does not hold manure.

No. 248 is from a soil stratum three feet thick. The soil is so light that the finer particles of it are carried away by high winds.

Nos. 206 and 209 are typical of the soils producing the long-leaf pine. This soil is much improved by an admixture of the subsoil No. 209, which enables it to hold manure.

No. 219 is a cotton upland soil of the best quality, found in Western Mississippi and Tennessee.

No. 397 is the same soil of a second rate quality. These lands are easily washed into gullies on account of their lack of perviousness to water. They also easily swell up in contact with water, and become thereby readily diffused. The denudations produced by heavy rains are rapidly destroying the lands covered by these soils.

No. 173 is a sedimentary or residual subsoil of the cretaceous prairies of Northeastern Mississippi, forming a stratum from three to seven feet thick.

[78] Association for the Advancement of Science, Portland (22nd) meeting, 1873: 72.

Silt Analysis of Mississippi Soils and Subsoils.

	Designation of materials.	Diameter. (Millimeters.)	Velocity (hydraulic value). Millimeters per second.	Drift.	Upland.										Mississippi bottom.						
					Yellow loam.							Tertiary.			Champlain.		Modern.				
					Sandy.			Loam.			Clay.				Swamp river.		River deposit.			Delta.	
				238	248	165	206	209	397	219	173	230	246	196	390	237	368	377	395		
				White pipeclay, Tishomingo Co.	Tallahoma subsoil Jasper Co.	Low Flatwoods soil. Chickasaw Co.	Pine Hill soil. Smith Co.	Pine Hill subsoil. Smith Co.	Oxford subsoil Lafayette Co.	Table Land subsoil. Benton Co.	Prairie subsoil Monroe Co.	High Flatwoods soil. Pontotoc Co.	Red Hills subsoil. Attala Co.	Hog Wallow subsoil. Jasper Co.	Buckshot soil. Issaquena Co.	Loess Claiborne Co.	Tallahatchie soil. Panola Co.	Prairie subsoil. Sunflower Co.	Dogwood ridge soil Coahoma Co.	Southwest pass. Plaquemine Parish.	Southwest mudlump Plaquemine Parish.
1	Coarse grits	1.0 to 3.0			6.94	2.90	0.36	0.36		0.23	2.10	0.33	1.97	0.83	0.09	0.24	0.09				
2	Fine "	0.5 to 1.0			17.65	6.96	2.98	0.83				0.35		1.19	0.05						
3	Coarse sand	0.40	64		18.81	2.81	6.62	6.21		1.47			0.72	1.96		0.37	0.04	0.32	0.15	18	0.10
4	Medium "	0.30	32	0.06	10.16	4.41	7.75	3.38	0.79	2.33	0.62		2.32	1.64	0.36	0.61	0.05				
5	Fine "	0.16	16		2.66	3.13	3.01	3.85		1.17			2.09	0.88		0.93	0.21	2.97		0.47	5.02
6	Finest "	0.12	8	0.08	1.66	2.02	1.59	1.49	0.18	0.78	0.20	0.23	0.70	0.26	0.31	1.65	1.30	2.41	3.74	7.03	3.68
7	Dust "	0.072	4	0.02	1.02	2.23	1.19	0.64	0.78	0.76	1.26	0.18	1.29	0.19	0.27	1.95	2.68	16.90	21.49	12.38	5.34
8	Coarsest silt	0.047	2	0.04	0.88	5.06	3.56	2.63	3.56	9.79	2.92	1.61	1.81	2.49	1.56	14.25	9.38	19.79	21.83	13.27	10.09
9	Coarse "	0.036	1	0.08	1.96	9.67	6.50	5.40	13.12	7.26	7.36	2.66	3.60	3.67	2.23	16.20	9.88	13.90	14.01	15.87	5.58
10	Medium "	0.025	0.5	0.08	7.89	14.18	13.97	7.77	16.64	13.14	8.81	9.13	2.73	5.39	3.68	20.08	20.37	4.27	9.93	8.25	9.54
11	Fine "	0.015	0.25	2.00	8.40	22.03	14.20	16.65	27.28	15.07	7.85	26.64	13.30	10.31	8.97	5.59	19.79	1.89	9.58	7.26	8.01
12	Finest "	0.008	<0.25	21.15	15.53	15.62	29.36	37.75	18.87	26.50	35.22	32.35	25.33	24.18	38.19	33.38	25.30	30.08	8.65	19.67	34.46
13	Clay		<0.0023	74.65	8.63	7.86	4.58	10.70	17.23	19.19	33.16	25 48	40.25	47.03	44.30	2.51	9.64	5.51	10.35	12.20	18.18
				98.16	99.28	98.68	95.67	97.77	98.35	97.65	99.50	97.87	96.11	100.00	100.01	97.74	98.73	98 04	99.72	96.58	100 00
	Compactness (resistance to tillage)			97.80	32.56	45.33	48.14	45.10	63.38	60.82	69.77	84.47	78.88	81.52	89.46	41.48	54.63	37.48	28.57	39.13	60.65
	Porosity			0.36	59.55	40.40	37.89	47.13	20.23	26.04	17.04	6.40	39.18	10.12	4.87	38.44	23.63	58.25	61.50	49.20	28.81
	Hygroscopic moisture (+7° to +21°)			9.09	1.80	3.36	2.48	7.69	8.79	7.21	11.35	9.33	18 60	14.48	14.31	4.18	6.12	5 68	3.95	. .	. .
	Ferric oxid			0.13	1.10	(1.45)	1.25	4.15	2.53	5.11	5.42	(5.90	10.50	4.00	(5.82)	3.27	2.58	2.31	2.69	. .	. .

No. 230 is a residual soil which is formed by the disintegration of the old tertiary clays. It yields good crops only in very favorable years, and is easily injured both by wet and dry seasons.

No. 246 is a soil of the same origin, but is more easily tilled than the foregoing, does not crack, but becomes very hard when dried slowly. Its superiority to the former soil as regards tillage consists in the presence of the large amount of iron and lime.

No. 196 is a typical heavy clay soil; is better suited for the potter than the farmer. It cracks on drying, whence its popular name. On the accession of rain the edges of these cracks crumble and fall, until finally the lumpy surface is produced which is locally known as hog wallows.

No. 390, the richest soil of the Yazoo Bottom, seems to have a physical composition like the preceding one. Its superiority is due not only to the increased quantity of plant food which it contains, but to its property of crumbling on rapid drying. Even when plowed wet, on drying each clod crumbles into a loose pile resembling buck-shot; whence its name. It is strongly calcareous.

As comparative data, are added the soils 365, 377, and 395, representing alluvial deposits, and two deposits from the Delta of the Mississippi.

262. Comparison of Osborne's Method with Hilgard's Method.[79] —The comparative results obtained by Osborne's method, beaker elutriation, and Hilgard's method, churn elutriation, are given in the following tables:

SOIL FROM EXPERIMENT STATION GARDEN, NEW HAVEN CONN.
SURFACE SOIL, BOILED TWENTY-THREE HOURS.

Diameter in millimeters.	Churn elutriation. Per cent.	Churn elutriation. Per cent.	Beaker elutriation. Average of four analyses. Per cent.
Removed by sieves	47.77	47.77	47.77
0.25–0.05	22.06	21.95	20.75
0.05–0.01	11.20	11.62	11.18
<0.01	9.82	9.14	10.72
Clay (difference)	2 32	2.69	2.75
Loss on ignition	6.83	6.83	6.83
	100.00	100.00	100.00

[79] Connecticut Agricultural Experiment Station Annual Report, 1886; 141.

SUBSOIL, BOILED TWENTY-THREE HOURS.

	Churn elutriation.		Beaker elutriation.	
Diameter in millimeters.	Per cent.	Per cent.	Per cent.	Per cent.
Removed by sieve...	39.33	39.33	39.33	39.33
0.25–0.05	33.61	30.83	32.35	32.95
0.05–0.01	10.91	12.25	10.32	10.37
<0.01	7.05	8.11	8.29	7.64
Clay..	5.02	5.40	5.63	5.63
Loss on ignition	4.08	4.08	4.08	4.08
	100.00	100.00	100.00	100.00

These analyses, conducted with sandy soils, agree quite as well as could be expected from two such different methods, and from the further fact that the beaker analysts were not accustomed to the use of the churn elutriator.

Elutriation of Clayey Soils.—Hilgard found that by churn elutriation no satisfactory results could be obtained on clay without long boiling and subsequent kneading of the finer sediments. Osborne examined a sample of clay by his method after previous boiling for 23 hours. When the sediments were examined by the microscope they were found to contain many aggregations of particles which broke into dust under the pressure of the thin glass slide-cover. These sediments were then gently crushed in the beaker with the help of a soft rubber stopper with a glass rod for a handle, the grinding together of the particles being, as much as possible, avoided. This pestling was continued with clear water as long as it occasioned turbidity. Comparison of the analyses shows that practically identical results were obtained on this soil whether it was boiled or not and indicates that the sediments are reduced to their elements by gentle pestling alone. For such soils, therefore, it is demonstrated that pestling is a much safer treatment than boiling. The same remark may be applied to the fertile prairie soil of Mercer County, Illinois, where boiling proved quite insufficient and in which the pestling process proved completely successful. The general conclusions arrived at from the results obtained by Osborne are as follows:

1. On sands and silts of pure quartz or similar resistant material Hilgard's method and beaker elutriation give practically identical results.

2. With coarse sands and silts upon whose grains finer matter has been cemented by silicates, etc., and with soils containing soft slaty detritus, the churn elutriator with preliminary boiling may give results too low for the coarse and too high for the finer grades. In these cases beaker elutriation with pestling yields more correct figures.

3. Some loamy soils containing no large amount of clay or of extremely fine silt, as well as prairie soils rich in humus, cannot be suitably disintegrated by twenty-four hours' boiling, but are readily reduced by pestling.

4. Beaker elutriation preceded by sifting, gives results in five or six hours with use of from two to three gallons of pure water, which, in churn elutriation, require several days and consume from eight to ten gallons of pure water.

5. Hilgard found that practically 0.25 millimeter is about the lowest velocity of water current per second available within reasonable limits of time in his elutriator. Such a current carries over particles up to 0.015 millimeter diameter and hence the silts of less dimensions cannot be conveniently separated by churn elutriation. In beaker elutriation there is no difficulty in making good separations at 0.01 millimeter and at 0.005 millimeter.

6. Beaker elutriation requires no tedious boiling or preliminary treatment and with careful pestling of the sediments gives, we believe, as nearly as possible, a good separation of adhering particles and at every stage of the process carries with it, in the constant use of the microscope, the means of testing the accuracy of its work and of observing every visible peculiarity of the soil. It is not claimed that pestling may not easily go too far, but in any case a good judgment may be formed of its effects and of the extent to which it is desirable to carry it.

7. In beaker elutriation the flocculation of particles occasions little inconvenience and does not impair the accuracy of the results, inasmuch as the flocculated particles are easily broken up.

263. Comparison of the Osborne with the Schloesing Method.—Schlösing's method has been compared by Osborne[80] with the beaker method of elutriation applied to the "sand" obtained by

[80] Connecticut Agricultural Experiment Station, Annual Report, 1887: 512.

the Schlösing method with results which show that this product is capable of separation into groups of very different value.

With the prairie soil from Mercer County, Illinois, the following results were obtained working on the original sample and the sand separated by the Schloesing process:

SCHLOESING'S METHOD.

	Per cent.
Calcium carbonate	0.88
Humus	1.57
Loss at 150° C.	4.42
Sand	82.86
Clay	7.86
	97.59

BEAKER METHOD.

	Schloesing's sand.		
	Dried at 150° C., per cent.	Ignited, per cent.	Original soil. Ignited, per cent.
Above 0.25 millimeter	0.12	0.10	0.92
0.25–0.05 millimeter	3.58	3.55	2.89
0.05–0.01 millimeter	42.69	41.87	42.86
0.01–0 millimeter	23.66	20.47	31.44
Clay	12.81	10.14	
Clay	....	....	7.40
Loss on ignition	....	6.73	14.49
	82.86	82.86	100.00

The "clay" obtained by the Schlösing method contained but little sand and in this respect the separation was satisfactory. The "sand," however, contained a considerable amount of clay. The data show that the textural character of the soil is greatly changed by the boiling with acids which the Schlösing method requires. The treatment with acid has disintegrated the particles of less than 0.01 millimeter diameter so that one-third of this portion appears as clay, according to the Hilgard method of estimating clay, which is the one employed.

As to the humus it may be noted that the loss in the analysis by Schlösing's method; *viz.*, 2.41 per cent, plus loss at 150° = 4.42 per cent, plus humus found = 1.57 per cent, plus carbon dioxid ($^{44}/_{56}$ of 0.88=) 0.69 per cent amounts to 9.09 per cent, while the loss on ignition which represents humus, carbon dioxid and water

is 14.49 per cent. The 5.40 per cent difference must evidently be, for the most part, humus which has escaped estimation by the Schlösing method, having been distributed among the sand and clay.

264. The Mechanical Determination of Clay.—Schlösing's method for the separation of the clay as stated by Osborne[81] is essentially one of subsidence for 24 hours from a volume of from 200 to 250 cubic centimeters of water, but of no specified height. Hilgard's conventional method requires the same time and a height of solution of 200 millimeters.

Such methods of separation assume, first, that most of the sand and, second, that little of the clay shall settle within the fixed time. That both of these assumptions are fallacious, the following experiments show. The clay obtained by twenty hours subsidence from thirty grams of brick clay is suspended in four liters of distilled water and allowed to settle out completely, which requires several days. The water is then decanted to remove all soluble matters, the jar again filled with distilled water, and the clay and fine sand again allowed to settle for several days. The upper three-quarters of the liquid are then decanted and made up to a volume of four liters, and this is allowed to stand several days, when a considerable sediment forms. A decantation is again made as before. The operations are repeated until the clay water has been so far freed from the clay as to become opalescent; then it first ceases to deposit any appreciable sediment. A microscopic examination of the several sediments thus collected shows them all to contain particles of sand. It appears, therefore, that only after the liquid containing the clay has become opalescent does it cease to deposit fine particles of sand as well as of clay.

Furthermore, the character of the true clay itself is so changed under certain conditions that it loses the property of remaining in prolonged suspension in water, as is shown by the following treatment:

A sample of clay which has been freed from particles of sand exceeding 0.005 millimeter diameter is suspended in water and

[81] Connecticut Agricultural Experiment Station, Annual Report, 1887, 157.

precipitated from it by freezing. It is then washed by decantation with alcohol and dried in the air. A portion of this clay is shaken with water and allowed to stand a few hours, during which time the greater part of it has settled. After decanting the water and suspended clay and repeating this process a few times, a very considerable part of the clay is left which will subside completely through 100 millimeters in a few hours. After standing under water for several months, only a small part of the clay has regained the quality of prolonged suspension. It has been found, however, that if this clay be pestled, this quality of prolonged suspension is restored to it to a very considerable degree. This fact seems to indicate that incipient flocculation is the cause of the more rapid sedimentation, but this is not mentioned by Osborne.

It is evident, therefore, that conventional methods depending on simple subsidence can give no accurate results because the ever varying amounts of finest sand and clay in different soils yield variable mixtures of the two when subjected to any simple course of treatment by elutriation and subsidence.

The method of persistent pestling and repeated subsidences and decantations continued until no further separation can be effected, although extremely tedious, is the only one which has so far yielded even approximately good separations on any of the clayey soils examined by Osborne.

A single subsidence of the clay water for 24 hours will free it from all particles of sand having a diameter greater than 0.005 millimeter, but in many cases a considerable amount of finer sand will remain in suspension for many hours or days.

On the other hand, the sediment formed during the 24 hours subsidence will not be free from clay, as may be easily seen by suspending it in water a second time and allowing it to stand again for 24 hours. Both Hilgard and Schlösing direct attention to these defects, but assume that they do not usually influence the results to a sufficient extent to deprive them of value. In many cases this is undoubtedly true, as, for example, in such soils as that from the garden of the Experiment Station, at New Haven, in which there is but little clay and fine sand; but in soils

of the opposite character, as in the North Haven brick clay where exact separations are most desirable, a very considerable error is thus inevitably encountered.

265. Effect of Boiling on the Texture of Clayey Soils.—Most investigators who have worked upon mechanical soil analysis advise boiling with water in order to detach clay and sand from each other and make a good separation of the several mechanical elements practicable or possible. In general, however, the instructions as to the time and manner of boiling are rather indefinite, and no definite research as to the effects of this treatment has been undertaken.

The practice of Hilgard, to boil 24 hours or even longer in case of adhesive clays, according to Osborne[82] appears to be objectionable in view of the dehydration and change of physical properties known to occur in case of many hydroxids, especially those of iron and aluminum, which may be present in the soil. It is a familiar fact that the hydroxids above named and many other amorphous substances when precipitated from cold solutions are more bulky and less easily washed upon a filter than when thrown down hot. It is also well known that their properties are considerably changed by warming or boiling with water. Heating with water to boiling for some hours or days gradually converts the bulky brown-red ferric hydroxid, which when precipitated cold and air-dried for 18 days has been found to contain 38 per cent. of water, into a much denser, bright red substance containing but two per cent of water. St. Gilles has also observed the partial dehydration of aluminum hydroxid from $Al_2O_3.5H_2O$ to $Al_2O_3.2H_2O$ by prolonged boiling.

The hydrate of silica and the highly hydrated silicates are most probably affected in a similar manner, and if such be the case, boiling would evidently change the constitution of clay in a very essential degree.

The following experiments throw light on this subject:

Ten grams of North Haven brick clay were boiled continuously for nine days with about 700 cubic centimeters of distilled

[82] Connecticut Agricultural Experiment Station, Annual Report, 18 87: 150.

water, in a glass flask of one liter capacity and furnished with a reflux condenser. Fifteen grams were boiled in the same manner for eight and one-half days. When the boiling was concluded, the soil was found to have assumed a granular condition, the clay and fine sand being collected into a mass of small grains resembling coarse sand and settling rapidly. One portion thus boiled was elutriated by the beaker method, the other by Hilgard's. The pestle was not used on either of those portions as it was desired to determine simply the effect of prolonged boiling. The separations thus accomplished are here compared with the elutriations of the same soil boiled 23 hours and of the pestled but unboiled soil.

	Hilgard elutriation.		Beaker elutriation.	
Diameter of particles.	Not pestled. Boiled twenty-three hours. Per cent.	Not pestled. Boiled nine days. Per cent.	Not pestled. Boiled eight and a half days. Per cent.	Pestled. Not boiled. Per cent.
By sieves	3.36	3.24	3.63	3.49
0.25–0.05	1.21	1.11	1.91	1.29
0.05–0.01	28.27	33.04	33.61	27.02
0.01–0	56.29	48.85	54.78	52.21
Clay	4.92	3.05	1.97	10.15
Loss on ignition	5.95	5.95	5.95	5.95
	100.00	95.24	101.85	100.11

It is observed that the eight to nine days boiling diminished the clay as determined by Hilgard's conventional method by from seven to eight per cent, increasing the dust by from two to three per cent, and the silt by about six per cent.

Under the microscope small, rounded, opaque, brown granules were seen in large numbers, which when pressed under the cover glass, broke up into a multitude of very fine particles.

From these experiments it would appear to be conclusively proved that too long boiling precipitates clay and thereby defeats the very object of the operation.

In these experiments the time of boiling was prolonged in order to bring out unmistakably the effects of this operation. If ebullition for eight or nine days reduces clay from ten to two per cent, increasing the 0.05-0.01 millimeter diameter grades by six per cent, it is evident that boiling for one day or a shorter time becomes a questionable treatment.

Further experiments made by boiling clay in a platinum vessel with a platinum condenser showed that this precipitation of the clay was largely if not wholly due to the salts extracted from the soil.[88].

When the clay has once been converted into the granular condition, considerable difficulty is experienced in restoring it to the state in which it is capable of prolonged suspension in water.

Osborne sums up the results of the studies reported, as follows:

1. The Berlin-Schöne method of elutriation gives fairly correct separations with sandy soils containing little clay or matters finer than 0.01 millimeter diameter, but on soils of fine texture, as loams rich in humus and clays, it gives results which are grossly inaccurate, the error on single grades amounting to from eight to fourteen per cent.

2. In respect of rapidity, economy of time, and ease of operation, the Schöne elutriation has no advantage over the beaker method.

3. Schloesing's method on its mechanical side makes no satisfactory separations, and the chemical treatment it employs is liable to alter seriously the texture of the soil.

4. The determination of clay by a single subsidence from any conventional depth or volume of water, or for any conventional time, is not a process certain to effect even a roughly approximate separation of the finest quartz grains from true clay.

5. Boiling with water must be rejected as a treatment preliminary to mechanical analysis, because it not only abrades and reduces the coarser sediments, but may dehydrate and coagulate the true clay and thus alter essentially the texture and grain of the soil.

266. Acceleration of Sedimentation.—Attention has already been called to the acceleration of sedimentation secured by invoking the aid of centrifugal force in the pendulous motion imparted to the elutriating vessels in the Bennigsen process. It is evident that other things being equal the time of sedimentation is inversely as the magnitude of the centrifugal force from the moment that force becomes great enough to neutralize the force of

[88] Report Connecticut Agricultural Experiment Station, 1888 ; Part II, 156.

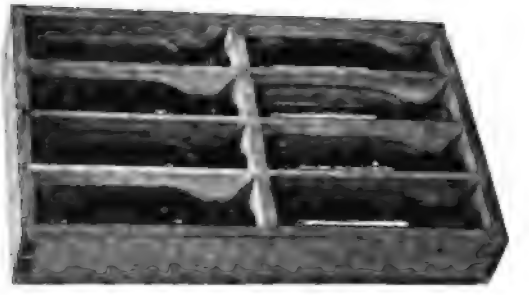


Fig. 43.—Shaker Tray Containing Bottles.

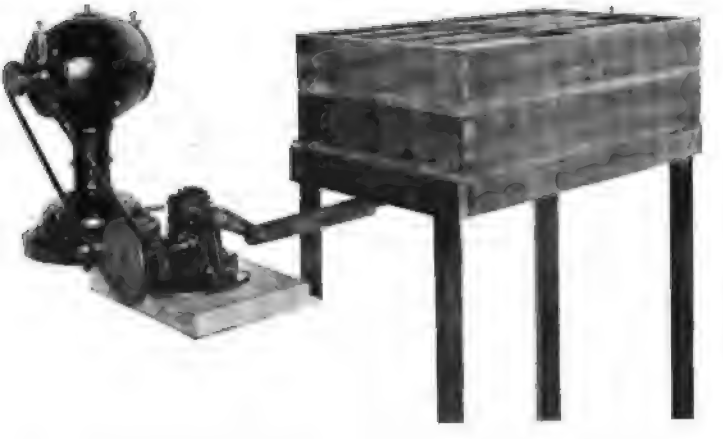


Fig. 44.—Mechanical Shaker Used in Preparing Soils for Mechanical Analysis.

gravity. By the use of a centrifuge it is therefore evident that the time of sedimentation may be greatly shortened. These principles underlie the process of centrifugal sedimentation elaborated by Briggs.[84]

Preparation of Sample.—Lumpy soils are reduced by a wooden rolling pin in preference to pestling or grinding, and passed through a sieve of two millimeters mesh. Gravel and other particles not passing the sieve are weighed. The part of the fine earth passing the sieve designed for mechanical analysis (from ten to 20 grams) is shaken with water for a few hours in a shaking machine shown in Figs 43 and 44. The five-gram samples are introduced into 250 cc. cylindrical round-bottomed sterilizing bottles, each containing approximately 75 cc. of distilled water. Ten drops of strong ammonia (sp. gr. = 0.9) are added to each bottle, which is then closed with a well-fitting rubber stopper. The bottles are placed in individual compartments in trays, each tray holding eight bottles, (Fig. 43), which corresponds to the number of samples usually analyzed at a time.

The shaker illustrated in the accompanying figure (Fig. 44), consists of a platform for carrying the trays, resting upon four flexible wooden supports, to which a reciprocating motion is imparted by a crank. Each tray is provided with a pin at either end which engages with the tray above it, so that six trays may be placed upon the shaker at one time, all easily accessible. The shaker is driven by a one-sixteenth horse-power motor which is belted to a fiber worm-reducing gear, provided with a crank to which the shaker is connected. The crank is five centimeters in length, and runs at 100 revolutions per minute. If the motor used with the machine is of the series of "fan" type, it is necessary to have a regulating rheostat, which is usually provided in the base of the motor, to adjust the speed when the shaker is not fully loaded. With a shunt wound motor, running at practically constant speed, a rheostat is not necessary, providing the reducing gear has been designed to drive the shaker at the proper speed.

This form of shaker is more convenient than one in which the platform is supported from above, since the supports do not inter-

[84] Bulletin No. 24, Bureau of Soils, The Centrifugal Method of Mechanical Soil Analysis; Briggs, Martin and Pearce.

fere with the removal of the trays. The use of thin steel or wooden supports, set with their planes at right angles to the direction of motion avoids the necessity of guides to prevent lateral motion, while little resistance is encountered to motion in the direction parallel to the plane of the crank.

THE CENTRIFUGAL MACHINE.

The primary requisite in making a mechanical analysis by the centrifugal method is some means of securing the high velocity required to throw down the suspended soil particles. An electric motor is most suitable for this purpose, if an electric lighting circuit is available. Large direct current series motors of the desk fan type are very satisfactory. Alternating current induction motors, of the desk fan type, are not sufficiently powerful to give satisfactory results. In case an alternating current circuit is the only one available, a belt driven apparatus used in connection with an induction motor of preferably one-half horse-power capacity should be employed.

The centrifugal apparatus illustrated in Fig. 45 consists of a 110-volt, 16-inch fan motor, mounted with its shaft in a vertical position, to which is attached a spider carrying eight trunnioned frames. The distance from the center of the motor shaft to the center of the trunnion screws is ten centimeters, and the depth of the trunnioned racks is 15 centimeters. The centrifugal tubes consists of large heavy glass test tubes 18x3 centimeters, which are supported to the trunnioned racks. The aperture in the upper ring of the support is made large enough to admit the test tube readily, while the opening in the lower ring is smaller than the tube, and is faced with a felt cushion on which the tube rests. It is important that the tubes should be thoroughly annealed, otherwise breakage is apt to occur under the strain to which they are subjected in the machine. To protect the operator from such accidents, a guard surrounds the movable portion of the machine.

The motor is provided with a rheostat in its base, giving four different speeds, which enables one to start the motor slowly and bring it gradually up to full speed. The machine when loaded and running at full speed requires about one minute to stop after the circuit is opened. To avoid this delay, the motor is provided

Fig. 45. Centrifugal Machine Used in Mechanical Analysis of Soils.

with a reversing switch, by means of which the direction of the current through the armature may be reversed, and the motor brought quickly to rest. Before stopping the machine in this way, the rheostat should be set at the first speed, and then slowly moved to the second or third speed, in order that the motor may not be subjected to too great mechanical and electrical strains in the reversing process. The microscopic method of examining the deposited silt is the same as in the other methods of silt separation.

267. Centrifugal Elutriator.—A combination of the principles of silt separation by a current of water and by centrifugal force is illustrated by the process of Yoder.[85] The object of the method is to be able to use a higher velocity of current for the separation of any one of the group particles and thus to accelerate the manipulation. The apparatus is shown in Figs. 46 and 47.

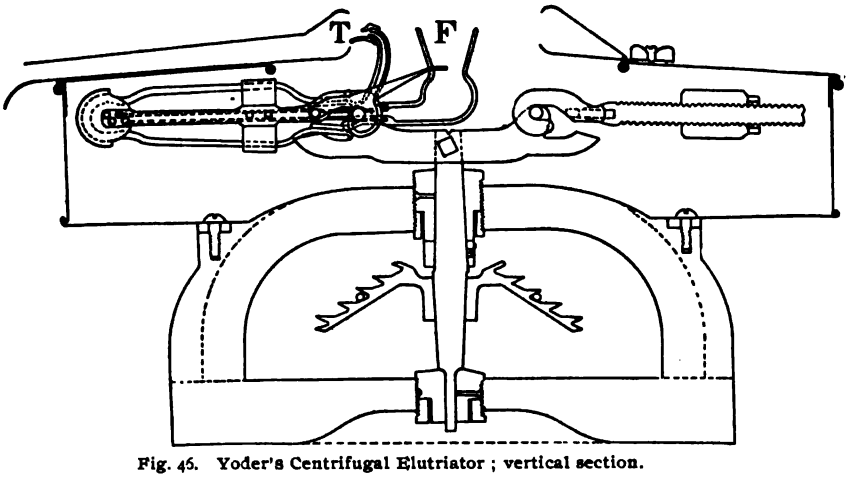


Fig. 46. Yoder's Centrifugal Elutriator ; vertical section.

Figure 47 shows the elutriator flush in longitudinal section, while Fig. 46 gives the details of construction.

The bottle is so designed that in the portion in which the separation is effected the velocity of the water column and the centrifugal force decrease in the same ratio, as the axis of the machine

[85] Bulletin 89, Utah Experiment Station. Bulletin 24, Bureau of Soils : 30 et seq.

is approached. A suspended particle is consequently subjected to a uniform force while in this portion of the bottle.

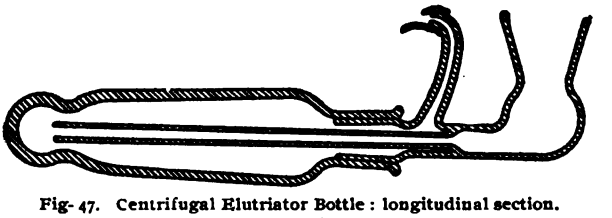


Fig. 47. Centrifugal Elutriator Bottle: longitudinal section.

It is not found practicable to stir the sediment in the bottom of the bottle by the inflowing current of water, consequently the material to be separated, suspended in a stream of water, is gradually introduced into the machine. The apparatus is used only in separating particles less than 0.03 mm. in diameter, this finer material being first separated from the rest of the sample by the beaker method. The water containing this fine material in suspension is run at a uniform rate through the machine, being introduced into the bottle through the funnel *F*, the axis of which coincides with the axis of the centrifugal machine, and coming out at the opening *T*, where it is caught by the spray collector shown in the upper part of figure. The size of the particles which pass out of the machine suspended in the water depends both upon the velocity of the stream of water and upon the speed of the machine.

A uniform flow of water containing the suspended material is secured in the following manner: The water containing the suspended material is placed in a funnel closed at the top, from which it flows into the machine as fast as air is admitted into the funnel. The air comes from a large closed bottle serving as an air chamber, into which the water flows from a mariotte apparatus, placed above, through a graduated valve that can be regulated at will.

The machine is first operated at such a speed that all particles larger than the superior limit of the group containing the finest material are precipitated to the bottom of the elutriator bottle. During this process some of the finest material is also carried down with some of the largest particles. The machine is then

stopped, the material in the bottom of the centrifugal bottle again suspended in water, and the operation repeated with the machine running at such a speed that the soil grains belonging to the group of coarsest particles will alone be precipitated. This process is continued until a sharp separation is obtained. The same procedure is followed for the other separations.

This method of separation has not been subjected to trial by the author of this treatise. It appears to introduce into the methods of silt separation a somewhat complicated piece of apparatus, novel in structure, but apparently of no great practical benefit.

268. Method of Sjollema.—This method is based on the principle of separating by centrifugal force the fine particles of the soil suspended in a thoulet solution of 2.51 specific gravity.[86] The inventor has improved his original method in several respects. The thoulet solution (described further on) has been replaced by a mixture of bromoform and chloroform of the same specific gravity.[87]

The centrifuge employed is similar to those used in the analysis of urine. By this device the clay and sand are separated, the former, at the end of the operation, being found on top, and the latter at the bottom of the liquid. It is evident that flocculated particles of clay attached to the heavier sand particles would be found at the bottom of the liquid, and therefore the separation could only be theoretically accomplished in a condition where the particles both of clay and sand are perfectly segregated.

The process is conducted as follows:[88]

Soil which contains much sand or undecomposed mineral matter is rubbed in a mortar with water. The liquid after standing a short time is poured off and this treatment is repeated several times. Care is taken not to break up the grains during the pestling. The portions poured off are evaporated nearly to dryness on a water-bath. The residue is stil further dried in a desiccator, placed in a mixture of bromoform and chloroform of a specific gravity of 2.5 and centrifuged for two or three minutes. The greater part of the sand is separated by this treatment. After the

[86] Chemiker Zeitung 1895, **19** : 2080.

[87] Proceedings of the 4th Congress of Agriculture, Paris, 1900, **2** : 132.

[88] Die landwirtschaftlichen Versuchs-Stationen, 1900, **53** : 71.

operation the vessels containing the mixture are left at rest for a short time during which suspended particles go to the bottom or come to the top.

The separating fluid carrying the lighter particles is thrown upon a filter which retains the colloidal substances which are subsequently washed with ether, dried and removed from the filter. The colloid mass is purified by moistening with water, rubbing in a mortar as before, the moisture nearly driven off and dried as before.

It is again submitted to centrifugal action, but with such addition of chloroform to the separating liquid as to reduce the specific gravity to about 2.32, which is very nearly that of the colloid substance itself. If the microscope still reveals particles of sand in the colloid the treatment above outlined is to be repeated.

269. Methods of Measuring the Diameter of Silt Groups.—During the progress of separation of the groups of silt particles the size of the average particle is determined from time to time by the microscope. A drop of the water in which the particle is suspended for the time being is removed to the stage of the microscope by sucking it into a small glass tube. Attention should be paid to the desirability of getting the sample from near the center of the body of the liquid in which the particles are suspended.

After placing the cover glass over the drop of water carrying the particles the slide is brought into the field of vision and the diameters of the best formed fragments determined with the micrometer. A number should be measured each time and the average diameter computed. When this average falls very near the mean theoretical size of the group the separation may be regarded as ended. Distorted or unusual forms should be omitted in the measurement and these should be regarded as having the same hydraulic value as the spheroid or regular forms measured. Further details respecting the microscopical examination will be given in another place.

270. Methods of Tabulation.—In the United States the chief methods of tabulation are those proposed by Hilgard, Whitney and Osborne, which have already been illustrated. Hopkins has

proposed a method of tabulation of results based upon the relation of the $\sqrt{10}$ times that of the inferior group.[89]

The numerical value of the $\sqrt{10}$ is nearly 3.2 and this number is used as the multiplier for each group above the smallest, excluding clay. In Hopkin's scheme the smallest group of particles has a diameter of .001 millimeter or less.

A comparison of the different methods of tabulation is given in the following table:[90]

SYSTEMS OF GROUPING EMPLOYED IN MECHANICAL ANALYSIS.

Number of group.	Hilgard. mm.	Osborne mm.	Bureau of soils. mm.	Hopkins. mm.
(1)	3.0	3.0	2.0	1.0
(2)	1.0	1.0	1.0	0.32
(3)	0.5	0.5	0.5	0.1
(4)	0.3	0.25	0.25	0.032
(5)	0.16	0.05	0.1	0.01
(6)	0.12	0.01	0.05	0.0032
(7)	0.072	(?)	0.005	0.001
(8)	0.047	....	....	....
(9)	0.036	....	....	....
(10)	0.025	....	....	....
(11)	0.016	....	....	....
(12)	0.010	....	....	....
(13)	(?)	....	....	....

There is little practical advantage in increasing the number of groups, however important it may be in a detailed study of a soil. The chief agronomic questions relating to the composition of a soil are answered by the determination of the parts that pass a 2, 1 and .5 millimeter sieve and by dividing the fine earth from the last mentioned sieve into clay remaining in suspension for 24 hours and into three or four intermediate groups.

271. General Conclusions.—The methods of Hilgard and Osborne have been given in detail and largely in the descriptive language used by the authors. The other methods of elutriation in use in other countries have also been described. For practical use the methods of Hilgard and Osborne are to be preferred to all others. For simplicity and speed the Osborne method has the preference over the Hilgard. For rigid control of the work the

[89] Bulletin 56, Bureau of Chemistry : 64.

[90] Bulletin 24, Bureau of Soils : 33.

Hilgard method leaves little to be desired. The effect of long boiling on clay pointed out by Osborne would suggest that the boiling process preliminary to the Hilgard method be made as short as possible. It would seem that the churn attrition in the Hilgard method might well be regarded as a substitute for the soft pestling of the Osborne process, and any prolonged boiling in the former method might be safely omitted. When carefully carried out, the results of the Hilgard and Osborne method are fairly comparable.

272. Distribution of Soil Ingredients.—The distribution of the soil ingredients in the sediments obtained in silt analysis is illustrated in the following table:[91]

Hydraulic value . . . . Clay			<0.25 mm.		0.25 mm.		0.5 mm.		1.0 mm.		Other sediments.	Total in sediments.	Original soil.
Per cent. in soil 21.64			23.56		12.54		13.67		13.11				
	A	B	A	B	A	B	A	B	A	B			
Insoluble residue	15.96	4.35	73.17	17.29	87.96	11.03	94 13	12.72	96.52	12.74	13.76	71.89	70.53
Soluble silica	33.10	7.17	9.95	2.34	4.27	0.53	2.35	0.32	. .			10.36	12.30
Potash	1.47	0.32	0.53	0.12	0.29	0.04	0.12	0.01	. .			0.49	0.63
Soda	1.70	. .	0.24	0.06	0.28	0.04	0.21	0.02	. .			0.12	0.09
Lime	0.09	0.03	0.13	0.03	0.18	0.02	0.09	0.01	. .			0.09	0.27
Magnesia	1.33	0.29	0.46	0.11	0.26	0.03	0.10	0.01	. .			0.44	0.45
Manganese	0.30	0.06	0.00	0.00	0.00	0.00	0.00	0.00	. .	0.36	. .	0.06	0.06
Ferric oxid	18.76	4.06	4.76	1.11	2.34	0.29	1.03	0.14	. .			5.60	5.11
Alumina	18.19	3.97	4.32	1.04	2.64	0.33	1.21	0.17	. .			5.51	8.09
Phosphoric acid	0.18	0.04	0.11	0.02	0.03	0.00	0.02	0.00	. .			0.06	0.21
Sulfuric acid	0.06	0.01	0.02	0.01	0.03	0.00	0.03	0.00	. .			0.02	0.02
Volatile matter	9.00	1.33	5.61	1.43	1.72	0.23	0.92	0.29	. .			3 64	3.14
Total	100.14	21.64	99.30	23.56	100 00	12.54	100.21	13.67	. .	13.10		98.28	100.63
Total soluble matter.	75.18	. .	20.52	. .	10.32	. .	5.16	. .	. .	. .	. .	. .	. .
Total soluble bases	41.84	. .	10.44	. .	5.99	. .	2.76	. .	. .	. .	. .	. .	. .
Soluble silica in crude substance.	0.38	0.01	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0.19

A. Calculated on the amount of sediment. B. Calculated on the amount of soil.

The separation into soluble and insoluble constituents was effected in the above analysis by five days hot digestion in hydrochloric acid of 1.115 specific gravity.

It is seen from the above analyses that the clay is by far the richest in mineral constituents of all the ingredients separated in silt analysis, the amount in the clay being more than twice that of all the others combined. Its volatile matters are also the largest. The large amount of soda, however, is probably in part due to

[91] Loughridge, Proceedings American Association for the Advancement of Science, 22nd meeting (Portland, Me.), 1873; 81.

the sodium chlorid used in the precipitation of the diffused clay. The following points in regard to the distribution of the different ingredients are instructive:

1. The iron and alumina exist in almost identical relative proportions in each sediment, making it probable that they are in some way definitely correlated.

2. Potash and magnesia also exist in almost the same quantities, and their ratio to each other in all the sediments being almost constant seems to indicate that they occur combined, perhaps in some zeolitic silicate which may be a source of supply to plants.

3. Manganese exists only in the clay, a mere trace being found in the next sediment.

4. The lime appears to have disappeared in the clay, having probably been largely dissolved in the form of carbonate by the large quantity of water used in elutriation. Its increase in the coarser portions may be owing to its existence in a crystallized form not so readily soluble.

5. In a summary of the ingredients, it is seen that there is a loss in potash, magnesia and lime in the sediments as compared with the original soil; and this loss is doubtless due to the solution of these bodies in the water of elutriation.

A noteworthy fact shown in this table is the rapid decrease of acid-soluble matter in the coarser sediments; even what is dissolved from so fine a sediment as 1.0 millimeter hydraulic value, equal to a diameter of 0.04 millimeter, is in this case a negligible quantity. This suggests forcibly the inutility of introducing into chemical soil analysis, grains of as large a size as will pass a sieve of one millimeter aperture. The hydraulic value of these grains would be somewhat between 150 and 200 millimeters per second. While the exact results of the above analysis may not be applicable to all soils, yet the range is so wide that the systematic exclusion from chemical analysis of inert materials, by means of preliminary mechanical separation, seems likely to lead to important improvements in the interpretation of the results.

273. Percentage of Silt Classes in Different Soils.—The adaptation of a soil to different crops depends largely on the sizes of the particles composing it and consequently on the relative percentages of the silt classes.

The following table gives the mechanical analysis of some markedly different types of subsoils:[92]

Diameter, millimeters.	Conventional names.	Early truck. 1.	Truck and small fruit. 2.	Tobacco. 3.	Wheat. 4.	Grass and Wheat. 5.	Lime-stone. 6.
2–1	Fine gravel ..	0.49	0.04	1.53	0.00	0.00	1.34
1–0.5	Coarse sand ..	4.96	1.97	5.67	0.40	0.23	0.33
0.5–0.25	Medium sand.	40.19	28.64	13.25	0.57	1.29	1.08
0.25–0.1	Fine sand	27.59	39.68	8.39	22.64	4.03	1.02
0.1–0.05	Very fine sand	12.10	11.43	14.95	30.55	11.57	6.94
0.05–0.01	Silt.....	7.74	4.95	28.86	13.98	38.97	29.05
0.01–0.005	Fine silt	2.23	2.02	7.84	4.08	8.84	11.03
0.005–0.0001	Clay.....	4.40	8.79	14.55	21.98	32.70	43.44
		99.70	97.52	95.04	94.20	97.63	94.23
Org. matter, water and loss.		0.30	2.48	4.96	5.80	2.37	5.77

274. **Description of the Soils.**—Number one represents the very early truck lands of Southern Maryland. It is a light yellow sand, belonging to the Columbia terrace formation. Under an intense system of cultivation and heavy manuring with organic matter, good crops of garden vegetables are produced which mature very early, at least ten days or two weeks before the crops from any other part of the state. Under the prevailing meteorological and cultural conditions this soil maintains about five or six per cent of moisture, while a heavier wheat and grass soil maintains from 12 to 20 per cent. The truck soil is so loose and open in texture that the rain-fall passes through it very readily, and it is undoubtedly partly owing to this drier soil that the plant is forced to the early maturity which secures it from competition from other parts of the State and insures a good market price.

Number two represents the later truck and fruit lands of southern Maryland. These lands contain rather more clay than those just described; they are somewhat heavier and closer in texture, and are rather more retentive of moisture. This land gives a larger yield per acre than the one just described, and in every way crops make a more vigorous growth and development, but the crop is about a week or ten days later in maturing, and for this reason it brings a lower price in the market. It is much bet-

[92] Whitney, Bulletin 4, Weather Bureau : 60, 64, 65, 69, 71, 73.

ter land than number one for small fruit and peaches. These lands are altogether too light in texture for the profitable production of wheat, and it would cost altogether too much to improve them so that even a moderate yield of wheat could be obtained.

Number three is a tobacco soil of southern Maryland. The finest tobacco lands of this locality come between the truck and wheat lands in texture, and contain from ten to 20 per cent of clay. The lighter the texture of the soil and the less clay it contains, the less tobacco it will yield per acre, but the finer the texture of the leaf. The tobacco yields more per acre on the heavier wheat soils, but the leaf is coarse and sappy and cures green and does not take on color. It brings a very low price in the market and does not pay for cultivation. The crop on the lighter lands is of much finer quality; there is a smaller yield per acre but the leaf takes on a fine color in curing, and brings a much better price per pound. Wheat is commonly raised on these tobacco lands to get the after advantage of the high manuring, and because the rotation is better for the land than where tobacco is grown continuously on the same soil. The finest tobacco lands are, however, too light in texture for the profitable production of wheat. These lands belong to the neocene formation.

Number four is a type of the wheat soils of southern Maryland. These soils represent about the lightest texture upon which wheat can be economically produced under the climatic conditions which there prevail. They contain from 18 to 25 per cent of clay, and are much more retentive of moisture than the best tobacco lands. This type is about the limit of profitable wheat production. These soils will maintain about 12 per cent of water during the dry season. Garden truck is so late in maturing on these lands that there is often a glut in the market when the crop matures, and the crops often do not pay the cost of transportation. The lands are too light in texture for a permanent grass sod. They belong to the neocene formation.

Number five represents the heavier wheat soils of southern Maryland, belonging probably to a different period of the neocene formation and containing about thirty per cent of clay. This soil is much more retentive of moisture and produces very much larger crops of wheat than the last sample. It is strong enough

and sufficiently retentive of moisture to make good grass lands. It is too close in texture and too retentive of moisture for the production of a high grade of tobacco, or to be profitable for market vegetables.

Number six is from a heavy limestone soil of lower Helderberg formation. It is a strong and fertile wheat and grass land.

275. Interpretation of Silt Analysis.—There is evidently some connection between the size of the soil particles and the character of the crop best suited to a given mechanical type of soil. Early vegetables are hastened to maturity either in light, sandy soils or on the black vegetable soil of pond bottoms which has no relation whatever to the composition of the essentially mineral soils first described. Wheat and grass do not thrive well on sandy soils and a certain quantity of clay seems very helpful to such crops. But 'clay' is not merely particles of very small size, but rather such particles consisting essentially of silicates, especially of alumina. The only relation which the size of soil particles has to the total or available fertility is connected with the relation of the particles to the root system of the plant. Fine quartz sand, no matter how divided its particles might be, would not support vegetable life. It has been shown by studies in the yield of beets that soil fertility has no direct relation to mechanical structure, save as indicated above.[93] The chemical constitution of the fine particles therefore must be known before any definite idea of fertility can be acquired.

276. Number of Particles in a Given Weight of Soil.—The approximate number of particles in the soil can be calculated from the results of the mechanical analysis by the following formula:[94]

$$\frac{a}{\frac{\pi(d)^3\omega}{6}} \div \mathrm{A}.$$

Where a is the weight of each group of particles, d the mean diameter of the particles in the several groups in centimeters, w is the specific gravity of the soil, and A is the total weight of soil. for the specific gravity of ordinary soils, the constant 2.65 may be used.

[93] Bulletin 78, Bureau of Chemistry : 48.

[94] Whitney, Bulletin No. 4, Weather Bureau : 33.

The diameter d is taken as the means for the extreme diameters taken for any group, for instance, for the silt this would be 0.003 centimeter, which is assumed to be the diameter of the particles in that group. This formula can only give approximate values, as the number of separations in a silt analysis must necessarily be small, amounting usually to not more than eight or ten grades, on account of the time and labor required for closer separations. There is relatively rather a wide range in the diameters of grains within any one of these grades, and absolute values could not be expected without a vast number of separations, so that all the grains in each group would be almost exactly of the same size.

The clay group has relatively the widest limits, which is unfortunate, as this is the most important of all the groups on account of the exceedingly small size of the particles. The figure 0.0001 millimeter is taken as the lowest limit of the diameter of the clay particles. These particles have been heretofore assumed to be ultra-microscopic, but by the use of a microscope of high power with oil-immersion objective and staining fluids, it has been possible to define the clay particles in a turbid liquid which has stood so long as to be only faintly opalescent.

Pending more exact measurements, the figure 0.00255 millimeter has been used as the diameter of the average sized particle in the clay group.

277. **Mineralogical Examination of the Particles of Soil Obtained by Mechanical Analysis.**—The principal object of the mechanical analysis of soils as has already been set forth is the separation of the soil into portions, the particles of which have nearly the same specific gravity and hydraulic value. It is evident without illustration that particles of the same hydraulic value do not necessarily have the same size. The rate of flow of a liquid carrying certain definite particles does not imply that these particles are of the same dimensions. Of two particles of the same size and shape, that one which has the lower specific gravity, will be carried off at the lower rate of flow. At the end of the operation, therefore, the several portions of the soil obtained will be found composed of particles of sizes varying within certain limits, and of these particles the larger ones will tend to be composed of minerals of lower specific gravity, and

the smaller ones of minerals of higher specific gravity. Of the same mineral substance, the particles which are most irregular, exposing for a given weight the largest surface will be found to pass over at a lower velocity than those of a more nearly spherical shape. The same law holds good for particles falling through a liquid at rest, *i. e.*, the heavier and more spherical particles, weight for weight, will sooner reach the bottom of the containing vessel. To complete the value of a mechanical analysis, it becomes necessary to submit the several portions of soil obtained not only to a chemical but also to a mineralogical examination. Only the outlines of the methods of examining silt separates for mineral constituents can be given here and special works in petrography must be consulted for greater details.[95]

It is evident that the methods of separation and examination from a mineralogical point of view about to be described can only be applied to silts of the largest size. The finer silts can not be separated into portions of different specific gravities by separating liquids of varying densities on account of the slowness with which they subside, thus tending to adhere to the sides of the separating vessels and to form floccules which are not all composed of the same kind of mineral particles. While, therefore, these processes are more appropriately described in connection with the silts obtained by hydraulic elutriation, they can be applied with greater success to the fine particles passing the different sieves used in the preparation of the soil for analysis or to the finely pulverized soil as a whole.

The minerals which have contributed to soil formation, moreover, are better preserved in the larger silt particles and therefore more easily identified. While the desirability of securing like determinations in the finer silts is not to be denied, in the present state of the art the analyst must be content with the examination of the larger particles.

278. **Methods of Investigation.**—The chief points to be observed in the examination of the fine particles of soil are the following:

[95] Anleitung zur mineralogischen Bodenanalyse, Franz Steinreide Leipzig, published by William Engelmann, and Microscopical Physiography of Rockmaking minerals, H. Rosenbusch, Translated by J. P. Iddings, John Wiley & Sons, New York.

(1) the size and shape of the particles; (2) measurement of crystal angles; (3) separation into classes of approximately the same specific gravity; (4) separation by means of the magnet; (5) determination of color and transparency; (6) determination of refractive index; (7) examination with polarized light; (8) examination after coloring; (9) chemical separation. For many of the optical studies above noted, it is first necessary to prepare thin laminæ of the mineral particles and properly mount them for examination. For the purposes of this manual only those processes will be described which are essentially connected with a proper understanding of the nature of the soil particles. For the more elaborate methods of research the analyst will consult standard works on mineralogy and petrography.

279. **Microscopical Examination.**—The direct examination of the silt particles with the microscope should attend the progress of separation. Unless the particles obtained have the same general appearance, the separation is not properly carried on. Especially is the microscope useful to determine if the value of the silt separation is impaired by flocculation. Unless flocculation be practically prevented during the separation of the finest particles, many of these will be left as aggregates to be brought over subsequently with particles of far different properties. No special directions are necessary in the use of the microscope. The silt particles are removed with a few drops of water by means of a pipette, a drop of the liquid with the suspended particles is placed on the glass, covered and examined wtih a convenient magnification. A micrometer scale should be employed in order that the approximate sizes of the particles may be determined. A *camera lucida* may also be conveniently used for the purpose of delineating the form of particles of peculiar interest.

280. **Microscope.**—Any good microscope furnished with polarizing apparatus may be used for the examination of the silt particles and sections. For directions in manipulating microscopes the reader is referred to works on that subject. A special form of microscope for petrographic work is shown in Fig. 48. The base, upright pillars and arm are made of japanned iron. The stage is made in two forms, first, plain revolving, having silvered grad-

uations at right angles and second, a mechanical stage with silvered graduations on the edge with vernier and graduations for the rectangular movements. The mirror bar is adjustable and graduated and the mirror is of large size, plane and concave. The

Fig. 48. Microscope for Silt Examination.

double chambered box in the main tube carries the upper nicol prism (analyzer). The lower nicol prism (polarizer) is mounted in a cylindrical box beneath the stage to which it is held by a swinging arm. It is adjustable also up or down and is provided with a compound lens for securing converged polarized light. In

revolving the prism a distinct click shows the position of the crossed nicols.

The latest form of microscope used in the Bureau of Chemistry for this work is in addition to the usual attachments provided with a revolving analyzer for the detection of very low doubly refracting minerals, and a Schwarzmann scale for the measurement of optical axial angles. Another important accessory is a detachable-screw micrometer movable in the focal plane of the occular by means of a drum screw which with the most powerful objective lens records a drum interval of 0.00004 mm.[96]

281. Form and Dimensions of the Particles.—In order to study the contour of the fine silt particles, it is well to suspend them in a liquid whose refractive index is markedly lower than that of the particles themselves, and for this purpose pure water is commonly used. Care must be taken that not too many particles are found in the drop of water which is to be placed on the object holder and protected with a thin, even glass. The tendency to flocculation in these fine particles will make the study of their form difficult if they are allowed to come too close together. The size of the particles, or linear diameter, is to be determined by means of an eye-micrometer. This consists of a glass plate on which a millimeter scale is engraved with a diamond, or photographed. The millimeter scale is the one usually employed, each millimeter being divided into tenths. On microscopes designed especially for petrographic work the micrometer is fastened to the eyepiece, and so adjusted as to read from left to right, or at right angles thereto. Sometimes an eyepiece-micrometer has two scales at right angles so that dimensions may be read in two directions without change. With an eyepiece-micrometer, not the dimensions of the object, but those of its magnified image are read, and the degree of magnification being known, the actual size of the object is easily calculated. The actual measurements may also be obtained by placing in the field of vision, a stage-micrometer and determining directly, the relation between that and the eyepiece-scale. If, for example, the stage-micrometer is ruled to 0.01 millimeter, and the eye-micrometer to 0.1 millimeter, and one

[96] Bulletin 79, Bureau of Chemistry : 39.

division of the stage-rule should cover three divisions of the eye-rule, then the one division of the eye-micrometer would correspond to an actual linear distance of 0.0033 millimeter in the object. If the two lines of division in the two micrometers do not fall absolutely together, the calculation may be made as follows: suppose that six divisions, 0.6 millimeter, in the eyepiece correspond to nearly five divisions, 0.25 millimeter, in the stage piece. To get at the exact comparison, take ninety-six divisions of the eye-scale and they will be found to be somewhat longer than eighty-one and somewhat shorter than eighty-two divisions of the stage-scale. It follows therefore that

one division of the eye-scale >0.008438 millimeter, and
" " " " " " <0.008541 " ;

and, hence, one division of the eye-scale corresponds almost exactly to 0.008489 linear measure.

282. Illustrations of Silt Classes.—In figure 49 are shown the relative sizes and usual forms of a series of silt separates made by the beaker method.[97]

The particles represented in each class are not all strictly within the limits of size described. For instance, in the largest size (No. 1) are two particles at least which show a diameter of more than one millimeter. The particles in general, however, are within the limits of the class; *viz.*, one-half to one millimeter, and this general observation is true of all the classes. In the case of the finer particles, especially of clay, the tendency to flocculation could not be overcome in the preparation of the slides for the photographic apparatus. The clay particles are so fine as to present but little more than a haze at 150 diameters of magnification. The particles seen are, in most cases, aggregates of the finer clay particles. The larger particles show the rounded appearance due to attrition and weathering. It would have been more instructive could the particles of the different classes all have been photographed on the same scale, but this is manifestly impracticable. The lowest power which shows any of the clay particles to advantage is at least 150 diameters, and with the larger particles such a magnification could not easily have been secured.

[97] Photomicrographs made in Bureau of Chemistry by Dr. G. L. Spencer.

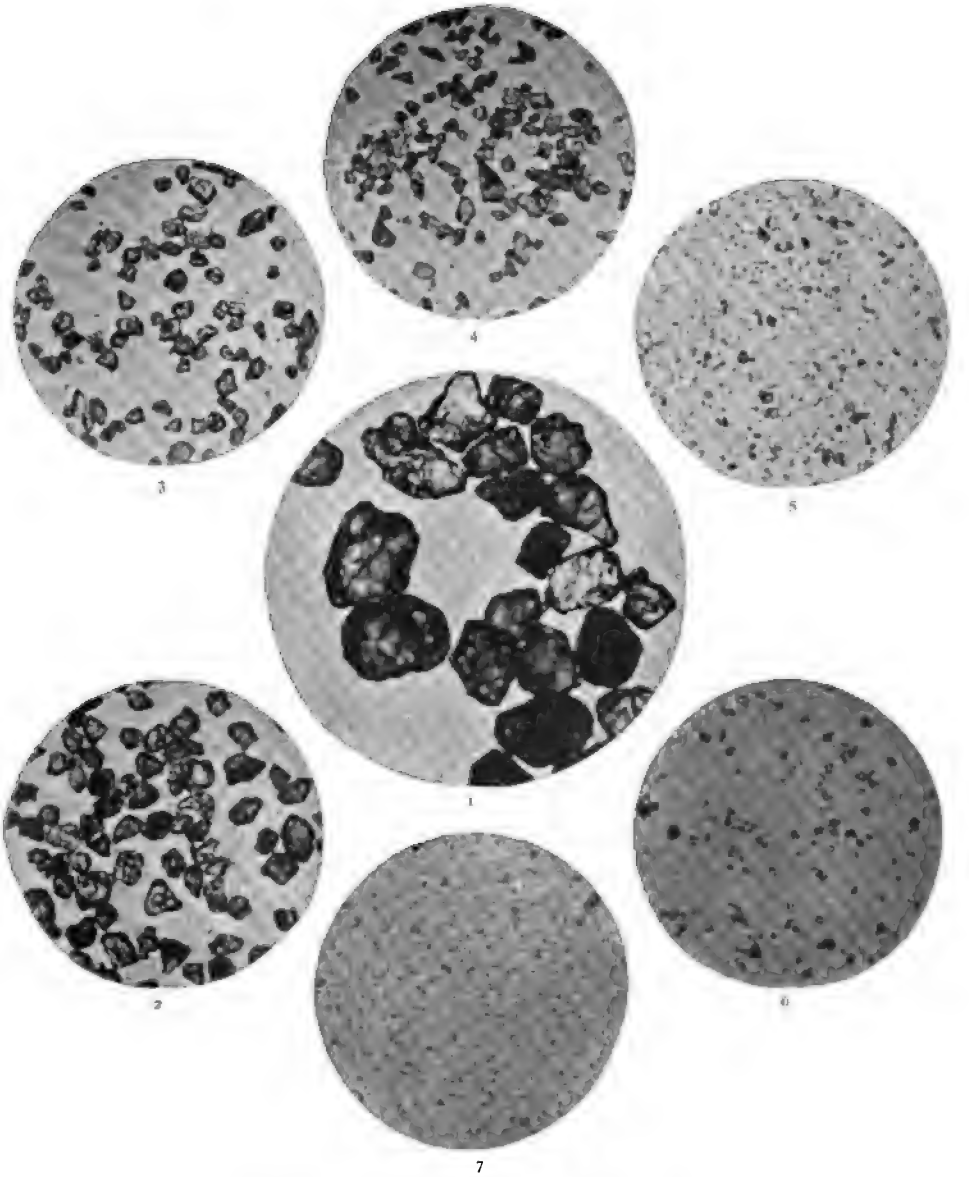


FIGURE 49. PHOTOMICROGRAPHS OF SILT PARTICLES.

No.	Diameter in mm.	Name.	Magnification. Diameters.
1	1.0 —0.5	coarse sand	× 10
2	0.5 —0.25	medium sand	× 10
3	0.25 —0.1	fine sand	× 10
4	0.1 —0.05	very fine sand	× 30
5	0.05 —0.01	silt	× 30
6	0.01 —0.005	fine silt	× 150
7	0.005—0.0001	clay	× 150

283. Measurement of Crystal Angles.—The fine silt particles rarely retain sufficient crystalline shape to permit of the measurement of angles and the determination of crystalline form thereby. The rolling and attrition to which the silt particles have been subjected have, in most cases, given to the fragments rounded or irregular forms which render, even in the largest silts, the measurement of angles impossible. For the methods of mounting minute crystals and the measurement of microscopic angles, the analyst is referred to standard works on mineralogy and petrography.

284. Determination of the Refractive Index.—For a study of the theory of refraction, works on optics should be consulted. The general principles of this phenomenon which concern the determination of the refractive power of fine earth particles are as follows: if a transparent solid particle is observed in the microscope imbedded in a medium of approximately the same refractive power and color, its outlines will not be clearly defined, but the imbedded particle will show in all of its extent the highest possible translucency. If, therefore, the form or perimeter of the particle is to be studied with as much definiteness as possible, it should be held in a medium differing as widely from it as possible in refractive power. For minerals, water is usually the best immersion material. On the other hand, when the internal structure of the particles is the object of the examination, it should be imbedded in oil, resin (Canada balsam), etc., or in some of the liquids mentioned below.

If particles of different refractive powers and the same character of surface be studied in the same medium, they will not all appear equally smooth on the field of the microscope. Some of the surfaces will seem smooth and even, others will appear rough and wrinkled. Those particles whose refractive index is equal to or less than that of the liquid appear smooth, because all the emergent light therefrom can pass at once into the environing medium. On the other hand, the surfaces of those particles which have a higher refractive power than the medium will appear roughened, because, on account of the unavoidable irregularities on the surface, many of the emergent rays of light must strike at the critical

angle and so suffer total reflection, and consequently those portions of the surface will be less illuminated, producing the phenomenon of apparent roughness above noted. In the case of any given particle, liquids of increasing refractive power can be successively applied until the change in the appearance of the surface of the particle is noticed. The refractive index of the liquid being known, that of the particle is in this way approximately to be determined.

The following liquids, having the indexes mentioned, are commonly employed:

Substance.	Refractive index.
Water	1.333
Alcohol	1.365
Glycerol	1.460
Olive oil	1.470
Canada balsam	1.540
Oil of cinnamon	1.580
Oil of bitter almonds	1.600
Oil of Cassia	1.606
Concentrated solution of potassium and mercuric iodid	1.733
Concentrated solution of barium and mercuric iodid	1.775

The solution of potassium and mercuric iodid may also be used for all refractive indexes from 1.733 to 1.334 by proper dilution with water.

The mineral particle may also be imbedded in Canada balsam and over it a drop of a liquid of known refractive power placed. By a few trials one of the liquids will be found having practically the refractive index of the particle under examination.

285. Examination with Polarized Light.—The internal structure of a mineral particle can often be determined by its deportment with polarized light. The theory of polarization is fully set forth in works on optics and will not be discussed here. The principle on which the utility of polarized light in the examination of soil particles rests is found in the information it may give in respect of crystalline structure. The structure of mineral particles which make up the bulk of an ordinary soil is, as a rule, so thoroughly disintegrated that all trace of its original form is lost.

Some particles may exist, however, in which there is no determinable element of shape and which yet possess an internal crystalline structure which the microscope with polarized light may be able to reveal.

An important feature of the microscopical examination of a mineral section is the determination of the relative abundance of the mineral components. To this end an ordinary fixed eyepiece having a square field is divided into 100 quadratic areas. With the aid of this device each square of which is the one-hundredth of the whole field the relative abundance of the minerals occupying the field can be determined with a great degree of accuracy, and entered on appropriate blanks.[98]

286. Staining Silt Particles.—The finer silts and clays before microscopic examination should be colored or stained. The methods used in staining bacteria may be employed for the clay particles.

Evaporation to dryness with a solution of magenta will often impart a color to the clay particles which is not removed by subsequent suspension in water. The harder and larger silt particles are not easily stained, especially if they be firm and undecomposed. On the other hand, if the particles be broken and seamed, and well decomposed, the stain will be taken up and held firmly in the capillary fissures. Valuable indications are thus obtained respecting the nature of the silt particles. Particles of mica, chlorite and talc are easily distinguished in this way from the firmer and less decomposed quartz grains.

Strictly-speaking, only the colloid or pectoid particles which have lost all traces of crystalline structure are sensitive to coloring agents. In a mixture of such particles with undecomposed mineral aggregates only the former will take the color; for example, methyl blue. In this way the use of a stain may indicate to a certain extent the physical state of the particles under examination.

The staining of the particles after ignition and treatment with acids gives better results than the direct treatment. Particles of carbonate which are stained with difficulty before ignition take

[98] Bulletin 79, Bureau of Chemistry : 39 and 58 et seq.

the stain easily afterwards on account of the decomposition produced by the loss of carbon dioxid. This is the case also with particles containing water of composition or crystallization.

287. Cleavage of Soil Particles.—A microscopic examination of the cleavage of soil particles may be useful in determining their mineral origin. The course followed by cleavage lines and their mutual position is dependent on the direction in which the separation of the mineral fragments takes place. The character of the microscopic fragments produced by crushing a soil particle is determined primarily by the system of crystallization to which it belongs. Perhaps the most distinguishing cleavage marks in soil particles will be found in fragments of mica and orthoclase. These characteristic forms are shown in Figs. 50 and 51. The first (Fig. 50) shows the pinacoidal cleavage in a fragment of mica. Fig. 51 illustrates the appearance of the cleavage lines in a fragment of orthoclase. Figs. 52 and 53 show the characteristic cleavage lines in fragments of epidote and titanite.[99]

288. Microchemical Examination of Silt.—The methods of quantitative chemical examination of silts will be given in another part of this manual. Certain qualitative and microchemical tests, however, are useful in identifying silt particles. For instance, any soluble iron mineral will be detected, even in minute quantity, by the blue coloration of the solution produced by the addition of potassium ferrocyanid. Manganese will be revealed by fusion with soda and saltpeter on platinum foil, in the oxidizing flame, producing the well-known green coloration due to the sodium manganate formed.

More valuable indications of the character of the fragments examined are obtained by microchemical processes. The best method of decomposing the silt particles for this purpose is by treatment with hydrofluosilicic acid. When the particles are composed of silicates, pure hydrofluoric acid is to be preferred.

The method of treatment is essentially that of Boricky.[1]

[99] Rosenbusch, Mikroskopische Physiographie, Stuttgart, 3rd Edition, 1892 : Plate x.

[1] Rosenbusch, Mikroskopische Physiographie : 259. Boricky, Elemente einer neuen chemisch-microskopischen Mineral- und Gestein-analyse, Prag, 1877.

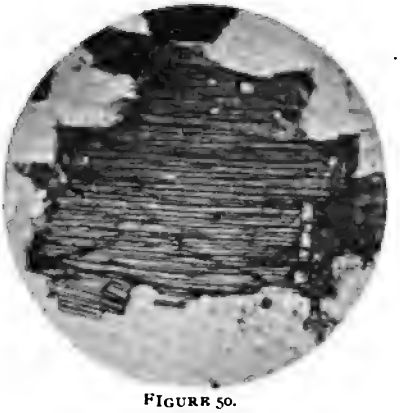


FIGURE 50.

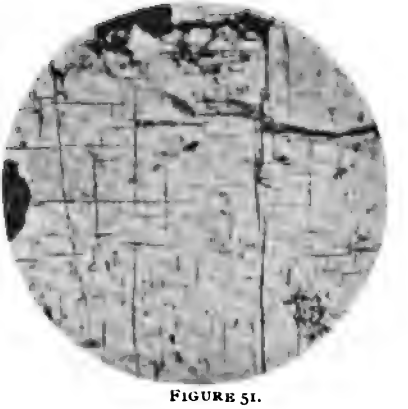


FIGURE 51.

FIGURE 52.

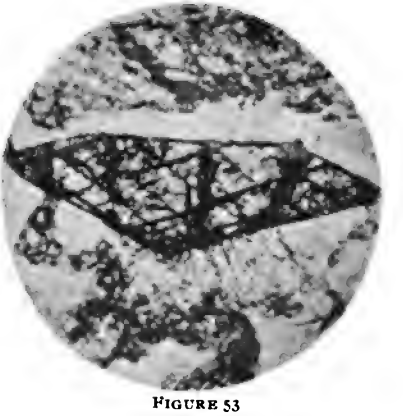


FIGURE 53

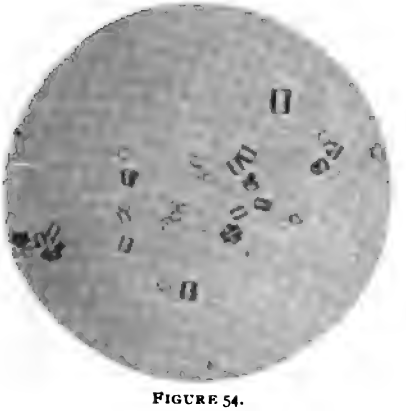


FIGURE 54.

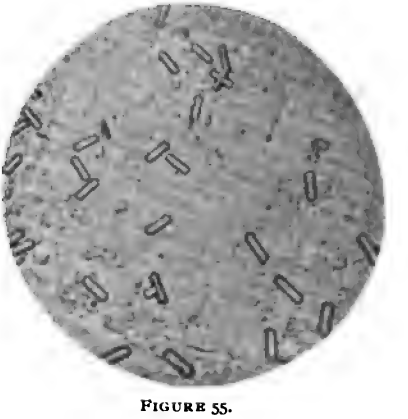


FIGURE 55.

Figures 50–53, show examples of the various degrees of perfection and relative positions of cleavage lines.

Figure 50, illustrates pinacoidal cleavage in mica from granite. Magnified thirty diameters.
Figure 51. A cleavage of orthoclase from augite syenite magnified twenty-seven diameters.
Figure 52. Cleavage of epidote magnified sixty diameters.
Figure 53. Cleavage of titanic magnified seventy-five diameters.
Figure 54. Sodium fluosilicate crystals magnified seventy-two diameters.
Figure 55. The same with aluminum fluosilicate magnified twenty-seven diameters.

The slide used is protected by a film of canada balsam, and a few of the silt particles are placed thereon, and fixed in place by slightly warming the balsam. Each particle is then treated with a drop of hydrofluosilicic acid, care being taken not to let the drops flow together. The acid must be pure, leaving no residue on evaporation. The acid should be prepared by the analyst from a mixture of barium fluorid, sulfuric acid and quartz powder, or the commercial article should be purified by distillation before using. The acid should be kept in ceresin or gutta-percha bottles and must be applied with a ceresin or guttà-percha rod. Each particle should be as completely dissolved as possible by the acid, and the rate of solution may be hastened by gentle warming, provided the heat is not great enough to remove the balsam and allow the acid to attack the glass. The univalent and bivalent bases present in the silt particles crystallize on drying as flousilicates. In case of a too rapid crystallization, the mass may be dissolved in a drop of water or of very dilute hydrofluosilicic acid, and allowed to evaporate more slowly. Some fragments need more than one treatment with acid to secure complete solution, and particles of mica may even resist repeated applications. In such a case the decomposition may be made in a platinum crucible with hydrofluoric acid, adding afterwards an excess of hydrofluosilicic acid and evaporating to dryness. The crystals may then be dissolved in a little water and a drop of the solution allowed to crystallize on the slide.

289. Special Reactions.—The number of microchemical reactions is very great, but there will be given here only some of the more important for silt identification.[2]

Sodium.—Sodium mineral fragments dissolved in hydrofluosilicic acid and dried give the combinations shown in Fig. 54. With sodium and aluminum the forms shown in Figs. 55 and 56 are obtained.[3] With an increasing amount of lime in the mineral, the crystals tend to become longer. For microscopic work it is not advisable to try to produce the tetrahedral crystals of the double uranium sodium acetate because the commercial uranium

[2] Rosenbusch, Mikroskopische Physiographie : 262 et seq.

[3] Figs. 54 to 57 inclusive are reproduced from the plates in Rosenbusch's work, cited above.

acetate often contains sodium and even the pure article will often take up sodium from the bottles.

Potassium.—Fragments containing potash give isotropic clear cubes, or octahedra of low refracting power, or combinations of these forms with each other and with rhombic dodecahedra. These crystals have the composition K_2SiF_6. Their forms are shown in Figs. 57 and 58. In case much sodium be present, the first crystals obtained may be strongly double-refractive rhombohedra, but on dissolving in water and allowing to recrystallize, the normal forms will be obtained. If the crystals be dissolved in hydrochloric or sulfuric acids, and treated with platinum chlorid, the characteristic yellow octahedral crystals of K_2PtCl_6 will be obtained. Ammonium and cesium compounds also give this reaction.

Lithium.—When fragments containing lithium are treated with the solvent mentioned, monoclinic crystals are produced on drying. These crystals dissolved in sulfuric acid and freed from calcium sulfate by treatment with potassium carbonate give aggregates of lithium carbonate resembling a snowflake. At a high temperature lithium solutions treated with sodium phosphate give spindle-shaped crystals of lithium phosphate. The double lithium aluminum silicofluorid is shown in Fig. 59. The ease with which traces of lithium may be detected by the spectroscope renders unnecessary any further description of its microchemical reactions.

Calcium.—Nearly all mineral particles, save quartz grains, contain calcium. When these particles are dissolved by treatment with hydrofluosilicic acid, they form on drying hydrated monoclinic crystals of calcium silico-fluorid ($CaSiF_6 + 2H_2O$). These crystals assume many forms, some of which are shown in Figs. 60 and 61. These crystals are easily decomposed by sulfuric acid, the well-known long prismatic crystals of gypsum taking their place. On treatment of silt particles containing lime with hydrofluoric and sulfuric acids, only a part of the lime passes into solution if the content thereof be large. Where but little lime is present and the sulfuric acid is in large excess, all the lime passes into solution and the characteristic gypsum crystals appear as in Fig. 62.

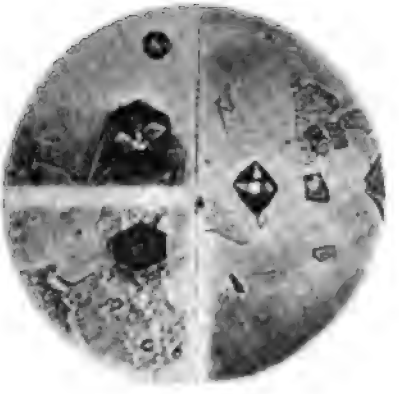


FIGURE 56.

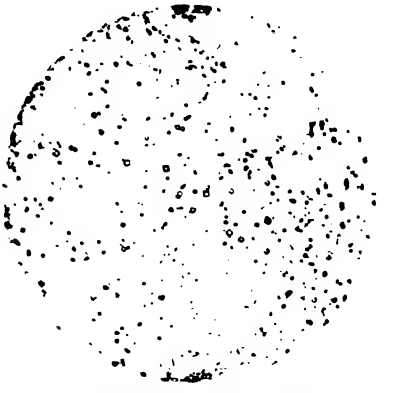


FIGURE 57.

FIGURE 58.

FIGURE 59.

FIGURE 60.

FIGURE 61.

Figure 56. Sodium and aluminum silicofluorid crystals magnified 100, 140 and 160 diameters.
Figure 57. Potassium silicofluorid crystals magnified 130 diameters.
Figure 58. Another preparation of the same magnified 140 diameters.
Figure 59. Lithium and aluminum silicofluorid crystals magnified 100 diameters.
Figure 60. Calcium silicofluorid crystals magnified 45 diameters.
Figure 61. Another preparation of the same magnified 42 diameters.

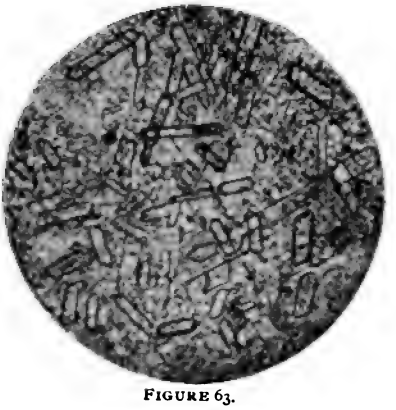


FIGURE 63.

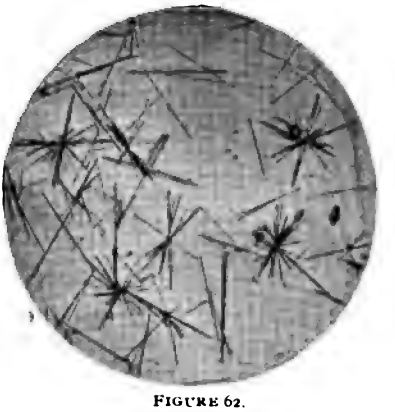


FIGURE 62.

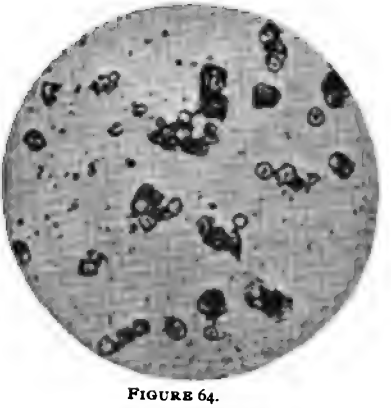


FIGURE 64.

FIGURE 65.

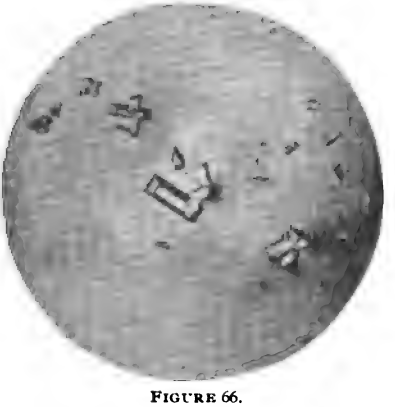


FIGURE 66.

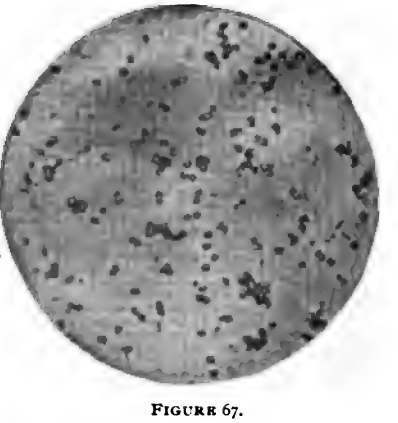


FIGURE 67.

Figure 62. Calcium sulphate crystals magnified twenty diameters.
Figure 63. Magnesium silicofluorid crystals magnified thirty diameters.
Figure 64. Cesium aluminum sulphate crystals magnified twenty diameters.
Figure 65. Ammonium magnesium phosphate crystals magnified ten diameters.
Figure 66. The same crystalized from dilute solution magnified thirty diameters.
Figure 67. Ammonium phosphomolybdate crystals magnified 140 diameters.

Magnesium.—Rhombohedral crystals of magnesium silicofluorid separate from the solution of particles containing magnesium in hydrofluosilicic acid. They have the composition $MgSiF_6 6H_2O$ and their common forms are shown in Fig. 63. Quite characteristic also are the crystals of struvite, $(NH_4MgPO_4 + 6H_2O)$, which are produced in a very dilute solution of the magnesium compound first obtained by carefully adding ammonium hydroxid and chlorid until a faint alkaline reaction is produced, and then placing a drop of dilute sodium phosphate at the edge of the solution. The crystals should be allowed to form slowly in the cold. Their form is shown in Fig. 65.

Barium.—From solution of fragments of barium-bearing minerals in hydrofluosilicic acid, no characteristic crystals are obtained. Treated with hydrofluoric and sulfuric acids the barium is left as sulfate. If this salt be dissolved in boiling oil of vitriol and a drop of the solution placed on the slide, a mixture of rectangular tablets and St. Andrew's cross-shaped growths will be separated before any crystals of gypsum which may be present appear. When strontium is present, the barium sulfate residue obtained by treatment with hydrofluoric and sulfuric acids should be fused with sodium and potassium carbonate, washed with water until the sulfuric acid is removed, the residue dissolved in hydrochloric or nitric acid, and the solution treated with potassium chromate. Pale yellow crystals of barium chromate are thus obtained, which resemble in form those secured by dissolving the barium sulfate in oil of vitriol. Strontium is not precipitated by this treatment. If potassium ferrocyanid be used instead of barium chromate with the hydrochloric acid solution, crystals of barium potassium ferrocyanid are formed of a bright yellow color and rhombohedric shape.

Strontium.—From a hydrofluosilicic acid solution, strontium crystallizes in columns or tablets of the monoclinic system as strontium siliciofluorid, $SrSiF_6$. On treating these with sulfuric acid, rhombic plates of strontium sulfate are formed, which serve to distinguish this element from calcium. On treatment of the particles of the original mineral with hydrofluoric and sulfuric

acids, the strontium remains in the insoluble residue. When this residue is treated with boiling oil of vitriol, rhombic plates of celestine are separated. If the residues above mentioned be dissolved by fusion with the alkaline carbonates, washed with water, dissolved in hydrochloric acid and treated with oxalic acid, octahedral crystals of strontium oxalate are formed.

Iron.—Mineral particles containing iron give crystals, when treated as is first described above, which are fully isomorphous with those obtained from magnesium. By moistening the crystalline mass with potassium ferrocyanid, the presence of iron is at once revealed by the blue coloration produced.

Aluminum.—No crystals containing aluminum are formed from the mineral particles containing this substance when dissolved in the solvent already mentioned. If, however, the gelatinous mass be dissolved in a little sulfuric acid and a fragment of a cesium salt added, beautiful crystals of cesium alum are obtained, illustrated in Fig. 64.

Phosphorus.—When a mineral fragment containing phosphorus is treated according to the usual analytical methods for securing the ammonium magnesium phosphate, crystals are obtained of the form shown in Figs. 65 and 66. A phosphatic fragment of silt may be identified when soluble by treatment with nitric acid and ammonium molybdate. On slowly drying, rhombohedral crystals are produced, yellow by reflected, and green by transmitted light. Their form is shown in Fig. 67.

290. **Petrographic Examination of Silt Particles.**—The larger silt particles and the minute fragments of minerals in the soil can best be studied in thin sections. For this purpose the following plan, proposed by Thoulet, may be used.[4] Mix the soil minerals in considerable proportion—Thoulet recommends ten per cent, but a greater percentage is often better—with zinc oxid and make into a paste with sodium silicate. The paste should be worked to the consistence of putty and then rolled into little tablets about one-eighth of an inch thick and an inch in diameter. After drying a day or two without heating, the tablets become hard enough

[4] Contributions à l'Etude des Propriétés physiques et chimiques des minéraux microscopiques, Paris, 1880 : 64 et seq.

to mount and grind like rock sections. These tablets are mounted in canada balsam on glass slides and ground as thin as possible with fine emery on the turn-table or glass plate, as rock sections are treated. As these tablets are not as strong as rock sections usually are, they require care in this treatment. Some of the grains also are apt to be torn out in the process of grinding and to compensate for this loss a number of slides should be prepared with each lot of soil minerals. When this operation has been successful, the optical properties of the various minerals can be studied as in rock sections.

As the iron oxid contained in the soils obscures the transparency of the minerals, it is well to treat a portion of the material under examination with hot hydrochloric acid for a short time to remove this oxid and then prepare slides with the cleansed material and compare results with the untreated. As the acid will dissolve phophates and carbonates, and will partly or wholly decompose some other minerals, the operator must be guided by his judgment in its use.

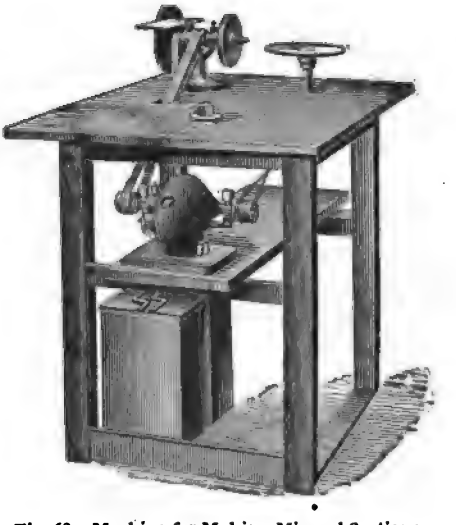


Fig. 68. Machine for Making Mineral Sections.

291. Machine for Making Mineral Sections.—A convenient apparatus for this purpose has been described by Williams[5] and is represented in Fig. 68. It is supported on a substantial table pro-

[5] American Journal of Science, 1893, 37, **45** : 103.

vided underneath with electric batteries and a motor for driving the cutting disks seen on the top. The table is three feet six inches square and two feet nine inches high.

The grinding apparatus consists of two circular disks of solid copper, nine inches in diameter, and three-eighths inch thick, which may be used alternately as different grades of emery are required. They are attached either by a screw or square socket to a vertical iron spindle which revolves smoothly in a conical bearing. The grinding disk is surrounded when in use by a large cylindrical pan of tin, which is not shown in the cut, which has an opening in its center to allow of the passage of the spindle.

The sawing apparatus consists of a horizontal countershaft placed on a different part of the table and connected with the motor by a separate belt. It carries at one end a vertical wheel of solid emery, and at the other an attachment, level-table and guide for the diamond-saw. A small water-can with spout, not shown in the cut, is suspended over the edge of the table to keep the saw wet when it is in use.

The machine is very conveniently driven by a storage battery when street circuits cannot be drawn on.

For the details of making mineral sections, the works on petrography may be consulted.

292. Separation of Silt Particles by Specific Gravity Solutions.—In silt separates the specific gravity of the different mineral particles present may vary from graphite (1.9—2.3) to hematite (5.2—5.3).

The following list gives the specific gravities of some of the more common minerals which may be met with in soils:

Gypsum	2.31
Albite	2.56–2.63
Quartz	2.65
Talc	2.74
Chlorite	2.78
Muscovite	2.85
Calcite	2.5 –2.78
Dolomite	2.90
Tourmaline	2.94–3.3
Biotite	3.01
Apatite	3.16
Pyroxenes	3.22–3.5
Epidote	3.39
Titanium minerals	3.48–4.75
Iron oxids	5.2 –5.3

The finest particles of silt are separated by gravity with great difficulty, inasmuch as they tend to remain suspended in the solutions for an indefinite period. With the coarser silts, however, useful data are often obtained by this method. The separation is preceded by extraction of the particles with hydrochloric acid to remove encrusted soluble matter, and by ignition to destroy any traces of organic matter. Those mineral matters which are soluble in acid or are changed by ignition must, of course, be sought for in separate portions of the silt.

293. **Thoulet's Solution.**[6]—The standard solution which was originally proposed by Sonstadt[7] is of such a density that particles of 2.65 specific gravity will just float thereon, using for this purpose a solution of about 2.7 specific gravity. The solution from which the above standard is prepared is made as follows:

One part of potassium iodid is placed in a beaker and one and one-quarter parts of mercuric iodid is placed on top of it. Then water is added in the proportion of ten cubic centimeters to 100 grams of the mixture, and after some time (12 to 24 hours), with occasional stirring, the salts will nearly completely dissolve. Filter from the undissolved residue and evaporate in a porcelain dish until crystals form on the surface of the liquid. Allow to cool, pour off the liquid from the crystals and evaporate the liquid for another crop. The first solution, after cooling, has a specific gravity between 3.10 and 3.20, the second a specific gravity of 3.28, practically the limit of density of the solution. The solution of 2.7 specific gravity and other densities are made by cautiously adding a few drops of water at a time and ascertaining the specific gravity by the Westphal balance or other convenient method.

The strong solution, according to Goldschmidt, may be prepared directly by using potassium iodid and mercuric iodid in the ratio of 1:1.24. Twenty-five cubic centimeters of water, 210 grams of potassium iodid, and 260 grams of mercuric iodid affords a solution of 3.196 specific gravity at 15°, on which fluorspar fragments will float. If the correct preparation of the two

[6] Rosenbusch, Mikroskopische Physiographie : 231.

[7] Chemical News, 1874, **29** : 127.

salts be maintained the solution can be diluted with water or concentrated by evaporation without losing its clear deep green color.

294. **Klein's Separating Liquid.**—A solution of cadmium borotungstate, of the composition $2H_2O,2CdO,B_2O_3,9WO_3 + 16H_2O$, has been proposed by Klein[8] for separating silt particles. This salt is obtained by dissolving pure sodium tungstate in five times its weight of water, adding one and a half parts of boric acid and boiling until complete solution takes place. On cooling, the borax is separated in crystalline form. The mother-liquor after the removal of the crystals is carefully concentrated by boiling. By stirring the cold solution, there is a further separation of sodium borate and polyborate. This operation is continued until glass will float on the mother-liquor. The salt in solution then has the following composition: $4Na_2O12WO_3,B_2O_2$. To this boiling concentrated solution, is added a boiling saturated solution of barium chlorid, in the proportion of one part of the chlorid to three parts of the original double tungstate. An abundant pulverulent precipitate is formed, making the whole mass mushy. The mass is filtered under pressure and well-washed with hot water. The residue is then suspended in hot water containing one part in ten of hydrochloric acid of 1.18 specific gravity. It is then evaporated to dryness in the presence of an excess of hydrochloric acid and decomposed, by which process hydrated tungstic acid is separated. The boiling mass is taken up with water and the boiling continued for two hours with occasional addition of water to take the place of that evaporated, and the tungstic acid separated by filtration.

From the solution, beautiful quadratic crystals separate having the composition $9WO_3B_2O_3,2BaO_2H_2 + 18H_2O$. These are purified by several recrystallizations and freed from any scales of boric acid by washing with alcohol. Any reducing action, revealed by a violet coloration of the crystals, can be avoided by adding a few drops of nitric acid. From a boiling solution of these crystals, the cadmium salt desired is obtained by treatment with the proper amount of cadmium sulfate solution to precipitate the barium. The barium sulfate is separated by filtration.

[8] Comptes rendus, 1881, **93** : 318.

The cadmium borotungstate is soluble in less than ten parts by weight of water. From this solution it is obtained in pure form by evaporation under a vacuum, or by carefully concentrating on a water-bath and cooling. A saturated solution of these crystals at 15° has a bright yellow color and a specific gravity of 3.28.

If a dilute solution of the above salt be carefully evaporated on a water-bath, any violet color which may be present disappears when the specific gravity reaches 2.7. If the evaporation be continued until a crystal of augite will float on the hot liquid, crystals may be obtained on cooling which, dissolved in as little water as possible, make a solution which will almost support olivine. If the two solutions be united, the specific gravity of the mixture is 3.30-3.36. The highest attainable specific gravity; *viz.*, 3.6, is produced by continuing the evaporation on a water-bath until the liquid will support olivine, and then allowing to stand in a closed place for twenty-four hours. The crystals of cadmium borotungstate thus obtained are freed as much as possible from the mother-liquor by drainage and then melted at about 75° in their own water of crystallization. A liquid is thus obtained on which spinel will float. The same concentration may also be obtained by careful heating on a water-bath. At its highest specific gravity this solution has an oily consistence and this renders its practical use in the separation of fine particles somewhat restricted. By filtering the liquor when a crystalline crust begins to form during evaporation, a cold solution of 3.360-3.365 specific gravity is obtained which is found practically useful. It has a higher specific gravity than Thoulet's mixture, is not injurious to any of the mineral particles, not even of iron with which it is brought into contact, but the trouble of preparing it is far greater than that of the mixture of mercuric and potassium iodids.

295. Rohrbach's Solution.—The solution of barium mercuric iodid recommended by Rohrbach[9] for this purpose was originally prepared by Suchsin, in St. Petersburg. The solution must be rapidly prepared on account of the tendency of the barium salt to decomposition. The solution is prepared by weighing rapidly 100 grams of barium chlorid and 130 grams of mercuric iodid,

[9] Rosenbusch, Mikroskopische Physiographie : 235.

mixing the two salts well in a dry flask and adding 20 cubic centimeters of water. The mixture is raised to a temperature of 150°-200° on an oil-bath. The formation and solution of the double salt are promoted by constant stirring.

After solution, the liquor is boiled for a few minutes and then evaporated on a water-bath until it will bear a crystal of epidote. On cooling, a small quantity of a yellow double salt is separated by crystallization and the resulting mother-liquor is dense enough to carry a fragment of topaz. Inasmuch as the liquor is filtered with difficulty, the clear mother-liquor should be separated by decantation after standing for several days. This solution has the disadvantage of not being dilutable with water, the addition of which causes a separation of red mercuric iodid. Were this solution not so easily decomposed, it would prove of high value in silt separation.

296. Braun's Separating Liquid.—In many respects the separatory solution proposed by Braun[10] is superior to those already mentioned. It is the commercial methylene iodid, CH_2I_2, which has at 16° a specific gravity of 3.32, at 5° of 3.35, and at 25° of 3.31. It is strongly refractive liquid having an index of 1.7466 for the yellow ray.

As a separating medium the liquid is open to two objections; *viz.*, first, it cannot be diluted with water and, second, it turns brown on heating or on long exposure to the sun-light.

When dilution is necessary, it should be accomplished with benzol or xylol. To bring the diluted liquor again to its maximum density, the benzol must be removed by evaporation, which causes a considerable loss in the liquid. When this substance becomes opaque, the transparency may be restored by removing the separated iodin by shaking with potash lye, washing with pure water, drying by the addition of pieces of calcium chlorid and filtering. The same result may also be reached by freezing and separating the liquid portion. The frozen portion on melting will have the density of the original liquid.

297. Separation in Silver and Thallium Nitrates.—A method of separating mineral fragments by means of a heavy solution prepar-

[10] Neues Jahrbuch für Mineralogie, Stuttgart, 1886, II : 72.

ed from silver and thallium nitrates has been described by Penfield.[11]

This mixture of nitrates was first prepared by Retgers, who showed that when mixed in molecular proportions these nitrates fuse at 75° in the form of a double salt to a clear mobile liquid having a specific gravity of more than 4.5 and capable, while melted of being mixed with water in all proportions.

The separation may be made in an ordinary test tube, while the salts are fused. All the particles heavier than 4.5 specific gravity will sink, and all those lighter float. Very few particles will be found suspended in the liquid. After cooling the tube is broken the solid salt holding the particles of different densities separated, fused and the mineral particles seasoned. Penfield recommends a more elaborate apparatus, the construction and operation of which are described in the paper cited.

298. **Method of Breon.**—Instead of a solution of a salt, Bréon[12] has proposed to use salts in a fused state for separating mineral particles. Lead and zinc chlorids may be used for this purpose in a melted state, having the specific gravities of 5.0 and 2.4, respectively. By mixing the molten salts in different proportions, any desired specific gravity between the extremes mentioned may be secured. The fusion is accomplished at 400° in a test tube. The silt is added gradually with constant stirring until a sharp separation is secured between the sinking and floating particles. After cooling, the tube is broken, the two parts separated, and the silt recovered by dissolving the mixed salts in hot water containing a little nitric acid. Only the coarser silts can be separated by this method. Fused silver nitrate, melting point 198°, specific gravity 4.1, has also been used for separation.

299. **The Separation.**—Forty cubic centimeters of the solution in the Thoulet process are placed in the separatory tube A, Fig. 69, together with from one to two grams of the silt and the stopper F inserted. The silt and separatory liquor are well mixed by blowing at I. The cock C is so opened and the blast of air so adjusted that no particles of the silt enter the space between C and

[11] American Journal of Science [3], 1895, **50** : 446.

[12] Bulletin, Société minéralogique, 1880, III : 46.

D during this operation. The tube G is connected with a vacuum apparatus by means of which any air particles adhering to the mineral fragmens are removed. The silt which sinks in the solution is removed after G has been disconnected by opening the cock C. Any excess of liquid that flows through C during this time is received in the bulb on the tube B. The cock C is closed and the separated particles washed into a beaker at H after opening D. Water is next added to the materials left in A in quantities previously determined to secure a given specific gravity and thus a second, a third, etc., separation secured. An intimate mixture

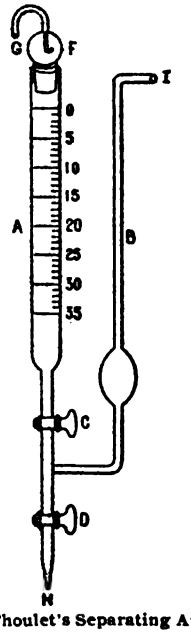


Fig. 69. Thoulet's Separating Apparatus.

of the solutions in A can be effected each time by closing D, opening C, and blowing through B in such a way that no liquid is allowed to pass through C, as already described.

The quantity of water to be added in each case to secure a given specific gravity is determined by the formula

$$v_1 = \frac{v(D - d)}{d - 1},$$

in which v is the volume of the solution, D its specific gravity,

and d and v_1 the specific gravity desired and volume of the water to be added.

Example.—Let the specific gravity of the original solution be 3.2, its volume thirty cubic centimeters, and the desired specific gravity of the new solution 2.85.

$$\text{Then } v_1 = \frac{30(3.2 - 2.85)}{2.85 - 1} = 5.68.$$

The desired specific gravity is therefore secured by adding 5.68 cubic centimeters of water, which is easily accomplished by means of the graduations on the tube.

According to Rosenbusch,[13] the calculated specific gravity as made above is not wholly reliable on account of the contraction which takes place. An empirical process is rather to be commended which consists in introducing a fragment of mineral of known or desired specific gravity and then adding water drop by drop until the fragment remains suspended in the mixture. Should too much water be added the necessary increase in density can be secured by adding a little of the strong solution.

300. **Method of Packard.**—A separatory funnel, according to Packard,[14] as suggested by Werveke,[15] may be safely used to hold the solution while separation is going on. As the lighter minerals form the bulk of soils, the heavier constituting only a small percentage, it is well to use a wide funnel holding as much as one-half liter for quantitative separations, because a large quantity of soil, say 100 grams, is necessary from which to recover the small quantity of heavy particles satisfactorily. The soil is introduced into the solution contained in the funnel, agitated, stirred with a glass rod, and allowed to stand some time. This operation may be repeated as often as desired. Separation is not absolute by this operation, the heavy and light particles being sometimes so united that they sink or float together according as one or the other preponderates. There are also particles having so nearly the same specific gravity as the solution that they remain indifferent to its action in any position. After separation has been

[13] Rosenbusch, Mikroskopische Physiographie : 232.

[14] Manuscript communication from R. L. Packard.

[15] Neues Jahrbuch für Mineralogie, 1883, II : 86.

effected, the heavy portion is drawn off through the stop-cock of the funnel and the lighter is skimmed off the top. Both must be thoroughly washed from the adhering heavy solution for further examination with the microscope, and by chemical, microchemical, and blow-pipe tests. One who has familiarized himself with the appearance of minerals in minute fragments under the microscope, in ordinary and polarized light, will be able to determine some minerals in that way. But for certain identification it is necessary to ascertain their optical properties as is done in the case of the minerals in thin sections of rocks.

Illustration.—The following example from the work of Packard will serve to illustrate the results of separating a soil by the specific gravity method:

One hundred grams of soil, residual clay from the Trenton limestone, were placed in the Thoulet's solution contained in the large separatory funnel. The heavy portion, after washing and drying, weighed 0.6886 gram, or 0.69 per cent. Of this, the magnet removed 0.1635 gram, or 0.16 per cent. This heavy material consisted of rounded yellowish and brown grains up to twenty-five millimeters in diameter, mingled with lustrous angular black grains which were seen under the microscope to be cubes with striated faces, cubes penetrating each other and aggregations of cubes. Combinations of cubes with octahedra and instances of the pentagonal dodecahedron were also observed. These forms, characteristic of pyrites, were also seen in the fine sand obtained as a residue on elutriating the same soil. As these crystals dissolved in hydrochloric acid, giving a strong iron solution, they were regarded as pseudomorphs of iron oxid after pyrites. The yellowish grains on treatment with acid left a grayish residue which contained some grains of quartz, but was not wholly quartz. The lighter portion of the soil, over ninety-nine per cent., which floated in the Thoulet's solution of 2.8 was next examined. It was colored red by the iron oxide which coated and adhered to the other minerals. It contained all the quartz, the feldspars if present, and the other minerals whose specific gravity is less than 2.8. It was examined by the microscope and found to consist largely of irregular grains of a mineral which acted

on polarized light, obscured somewhat by the iron oxid, and which was apparently quartz; and another mineral which was yellowish-brown in color and seemed to be dull and not transparent. Besides there was a large quantity of indistinguishable amorphous material. To clean these minerals the material was treated with hydrochloric acid to remove the iron oxid and other matter soluble in acid, when the quartz grains appeared transparent and gave interference colors in polarized light. But mingled with these were grains of the other mineral which now appeared grayish, dull, and without action on polarized light. The character of this mineral substance could only be determined by chemical analysis

301. Harada's Apparatus.—It is commonly held by analysts that in the subsidence of small particles it is advisable that the containing vessels have parallel sides, yet in the method just given, and in those about to be described, valuable results are obtained in a funnel or pear-shaped holder.

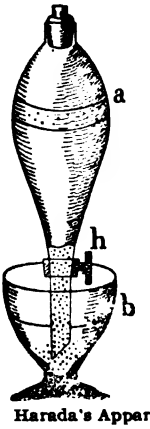


Fig. 70. Harada's Apparatus.

In the apparatus of Harada,[16] which is highly praised by many analysts on account of its simplicity and effectiveness, Fig. 70, the separating vessel *a* is made of thick glass furnished with a glass stopper above and a glass stop-cock *h* below. The separating liquid and silt are placed in the pear-shaped vessel *a*, the stopper inserted, and the whole well-shaken. As soon as a ring

[16] Rosenbusch, Mikroskopische Physiographie : 241.

of clear liquid is seen between the sinking and floating silt, the lower end of the apparatus is brought near the bottom of a conical glass *b*, the cock *h* opened and the heavy silt allowed to fall out. Very little of the liquor will flow out because of the air pressure. Should an air bubble enter the apparatus and be held at the stop-cock, it should be made to ascend by gently tapping. When all the heavy silt has passed into the conical glass, the cock *h* is closed and some water poured over the solution and silt in *b*. The separatory apparatus is now raised until the beveled end of it is in the water layer, when the water at once rises to *h* and thus washes all the silt particles adhering to the glass into *b*. The liquid in *a* may then be diluted by inverting the apparatus, adding the required amount of water through *h*, again shaken after closing *h*, and another separation secured as before.

This apparatus is somewhat easier to manipulate than Thoulet's but does not admit of the same exact quantitative dilution of the separating liquid.

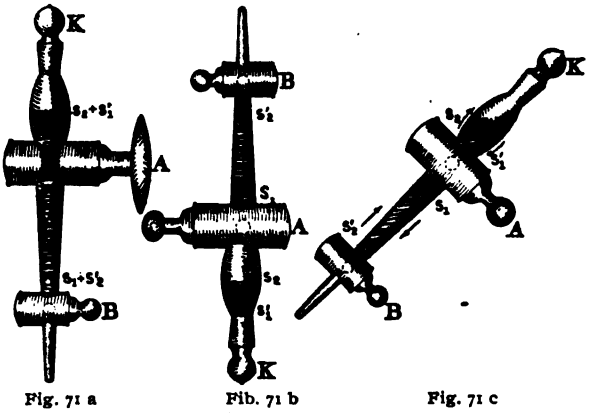


Fig. 71 a Fig. 71 b Fig. 71 c

Bröggers Apparatus.

302. **Apparatus of Brögger.**—All silt separations in narrow tubes are open to the objection of permitting more or less flocculation. Some of the lighter particles are thus carried down by the heavier, and, on the other hand, some of the heavier float with the lighter. This disturbing action Brögger[17] seeks to avoid by the

[17] Geologiska Föreningens i Stockholm Förhandlingar, 1884, 7 : 417.

following device, shown in different positions in Fig. 71, a, b, c. The length of the apparatus is forty-six centimeters, and its greatest diameter 3.5 centimeters. The opening in the large stop-cock A is the same diameter as that of the apparatus at that point. The cubical content of the apparatus with A open and B closed is about seventy-five cubic centimeters. In conducting the separation the cock B is closed, the separating liquid and silt introduced, A being open, the stopper K inserted and the whole well-shaken. In the first separation, the silt S_1, lying over B is contaminated with some of the lighter particles S'_2, while the lighter particles above A, S_2, are mixed with some of the heavier particles, S'_1. After closing A the apparatus is again well-shaken and inverted as in Fig. 71 b. The two parts of the silt will now undergo another separation as indicated. The apparatus is now carefully inclined as in c, when the various grades of silt will flow in the directions indicated by the arrows, but without mixing, passing each other on opposite sides of the apparatus. When the movement is complete, A is carefully opened, the apparatus still

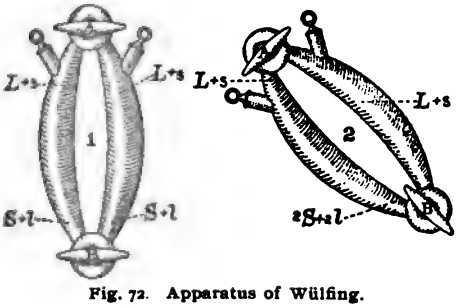


Fig. 72. Apparatus of Wülfing.

being held as in c, and the light silt formerly between A and B will flow above A, while the heavy silt above A will flow down and join the silt collected over B. This operation may be repeated until a perfect separation is affected. Finally B is opened and the heavy silt collected in a beaker, and the lighter silt then removed from the upper part of the apparatus.

303. **Method of Wülfing.**—A somewhat more convenient method of purifying the silt segregates and freeing them of mechanically occluded particles of differing specific gravities has been

proposed by Wülfing.[18] An elliptical ring of heavy glass tubing carries glass stop-cocks A and B, Fig. 72, at the two extremities of the ellipse, each arm of which is provided with a lateral glass-stoppered neck. The perforation in the stop-cocks has the same diameter as the ends of the ellipse. The apparatus has an interior content of about forty cubic centimeters. Thirty cubic centimeters of the separating fluid are introduced through one of the lateral apertures and brought to the same height in the two arms by opening the cock B. The silt is then introduced in equal quantities into each of the arms. The stoppers having been inserted, the whole is well-shaken. At the beginning of the separation, the apparatus being held in a vertical position 1 the lighter soil above and the heavier soil below are somwhat mixed by reason of flocculation and mechanical entanglement. At this point B is opened and the apparatus placed in the inclined position 2. The heavier particles $S + l$, on the right arm 1 are thus united with the same class of particles in the left arm 2 making $2S + 2l$. This operation is hastened by opening A and allowing the higher column of liquid in the right arm to pass into the left. The liquid in the left arm is allowed to rise to A. After all of $S + l$ in the right arm has passed into the left, B is closed, the apparatus then placed back in position 1 and inclined in the opposite direction until $L + s$ in the top of the left arm has been transferred to the $L + s$ in the top of the right, and the same quantity of liquid is found in each arm. The operation is then repeated and this continued until all $S + s$ is found in the bottom of the left arm and all $L + l$ in the top of the right arm.

Somewhat different forms of apparatus for conducting separations of this kind have been suggested by Laspeyres.[19]

304. **Separation with a Magnet.**—Particles of magnetic iron oxid are easily separated from the fine soil particles by means of a magnet. A strong bar or horseshoe magnet may be used. Electro-magnets are rarely necessary except for the separation of particles of feeble magnetic power. Particles of iron which may be found might owe their origin to the mortars in which the soil had

[18] Rosenbusch, Mikroskopische Physiographie : 243.

[19] Chemisches Centralblatt, 1896, 2 : 817.

been pulverized, or they might come from a recently crushed meteorite or magnetic ore. Some minerals, as limonite, after ignition are attracted by the magnet and it is advisable to subject a part of the sample to this treatment. The best method of separation consists in spreading the particles evenly on paper and gradually bringing the magnetic particles to one side by moving the magnet underneath.

305. Abundance of Mineral Compounds in the Soil.—The detection of mineral fragments in the soil by means of separation of the soil particles into groups by size and by specific gravity renders it more easy to distinguish the kinds of mineral fragments present by microscopic and microchemical means. Thus the nature of these fragments is revealed and additional knowledge of soil in respect of its original constitution obtained.

Delage and Lagatu have pointed out the very numerous kinds of minerals in soils.[20]

Carbonate of lime in two forms, hyolin quartz and one other variety, schists, muscovite and biotite micas, sericite, orthoclase and oligoclase feldspar, pyroxene, augite, amphibole, sphene, zircon, apatite, chlorite, serpentine, limonite and oligist iron minerals were found in a single sample of soil.

306. Color and Transparency.—But little can be learned from the color and transparency of the smallest silt particles, but these properties in the larger grains have considerable diagnostic value. Many minerals of distinct color appear wholly colorless in petrographic sections or in silt particles, as for instance, highly-colored quartz. On the other hand, even the smallest particle of chlorite will show its distinctive tint. The colors in some minerals are due to occluded matter not essential to their structure, and these foreign bodies would naturally escape when the crystal mass is reduced to an almost impalpable powder.

307. Value of Silt Analyses.—As in the case of chemical analyses a silt analysis of a soil which is not typical or representative has little value. On the other hand, a systematic separation of soils into classes of particles can not fail to reveal a definite correspondence of mechanical composition to physical soil properties.

[20] Comptes rendus, 1904, **139** : 1233.

The production of a crop is the result of certain environments, chief among which are temperature, moisture, and plant food. In a given soil the temperature is markedly affected by its physical state. It has been demonstrated in previous paragraphs that the circulation of moisture in the soil and its capacity to be held therein are chiefly functions of the state of aggregation of the soil itself. The availability of plant food in a soil is not measured by its quantity alone, but also by its state of subdivision. It is not therefore a matter of surprise that the fertility of a soil is found, *caetèris paribus*, to be commensurate to a certain limit with the percentage of fine silt and clay which it contains. It is true that two soils quite different in fertility, may have approximately the same silt percentages, but in such a case it is demonstrable that even in the poorer soil the measure of fertility is largely the percentage of fine particles in connection with its actual content of plant food. Many soils may have large quantities of plant food, but these stores, owing to certain physical conditions, are not accessible to the rootlets of plants. An illustration of this is seen in the use of concentrated fertilizers. It might seem absurd to suppose that the addition of 100 pounds of sodium nitrate would prove useful to a plat containing already a much larger quantity of nitrogen; but the nitrogen of the nitrate is at once available and its beneficial influences are easily seen.

The full value of silt analysis will only be appreciated when many typical soils from widely separated areas are carefully studied in respect of their chemical and physical constitution and the character of the crops which they produce.

PART FIFTH

ESTIMATION OF GASES HELD IN SOILS.

308. Relation of Soil Composition to Gases.—The power of a soil for occluding gases rests primarily on its composition as determined by silt analysis. The discussion of this part of the subject is so nearly related to that of the physical properties of the soil that it might properly have been included in that part of the work. Since, however, we deal in this part more with the determination of the gas constituents of the soil, it was deemed preferable to place it after the silt analysis and as introductory to the general estimation of the chemical constituents of the soil.

309. Occurrence of Carbon Dioxid.—Aside from the elements of the atmosphere by far the most important gaseous constituent of the atmosphere is carbon dioxid. The amount of organic matter in the soil is not necessarily an indication of the quantity of carbon dioxid when the organic matter is in excess. The percentage of carbon dioxid is only proportional to the amount of organic matter when this is in small quantities. Large quantities of organic matter do increase the amount of carbon dioxid, but the increase is not a proportional one, since a larger quantity of this gas in the air of a soil reduces the activity of the organisms which produce oxidation. Water and temperature have a great influence on the oxidation of the organic matter, which depends chiefly upon the activity of ferments of various kinds. The amount of free gas in the soil affords no certain indication either of the intensity of the action of oxidation or of the amount of organic matter. The carbon dioxid found in the soil may have its origin partly in the rain water which dissolves it from the atmosphere in subterranean sources or more frequently from the decay of the organic matter in the soil naturally or that which is added thereto in the application of organic fertilizers.

310. Absorption of Aqueous Vapor.—The power of a soil to resist drought depends largely upon its coefficient of absorption for

aqueous vapor. In general, clay soils are more absorbent than sandy ones, yet there is no direct connection between the amount of clay present and the absorbent power of the soil. Evidently the hygroscopic coefficient is largely controlled by the presence with the clay of the powdery ingredients which determine its looseness of texture, and it is found that the finer silts possess considerable absorbing power. The movement of aqueous vapor from the air to the soil or *vice versa* depends on the conditions of equilibrium which may obtain. Whenever these are such that moisture is attracted one way or the other, a movement will always be started towards the reëstablishment of equilibrium. It is evident that the relation of a soil to the air in so far as its ability to attract hygroscopic moisture is concerned depends largely on the size and chemical structure of its particles.

311. **Methods of Study.**—The study of the deportment of a soil with vapors or gases may be divided into two general classes. The first depends on the subjection of a sample of soil to the saturating influence of a given vapor or gas and measuring the amount thereof absorbed, either directly by increase of weight, or by the diminution in the amount of gas originally supplied. The maximum absorbent capacity of a soil under given conditions for a gas or vapor is in this way determined.

In the second class the determination consists in accurately estimating the amount of gas which is absorbed by a soil in natural conditions or *in situ,* thus giving the natural percentages of the gaseous constituents of the soil.

In the first case in general, the principle of the method depends upon the exposure of the soil for a given time under given conditions, to an atmosphere of the gas to be absorbed. The principle of the second class of determinations depends upon the extraction, usually by means of suction, from a given mass of soil of the gaseous matters therein contained. The general details of the methods of procedure for the first class are found in the following directions for manipulation:

312. **Determination of the Maximum Hygroscopic Coefficient.**—The fine earth, in Hilgard's method, is exposed to an atmosphere saturated with moisture for about 12 hours at the ordinary

temperature (60° F.) of the cellar in which the box should be kept. The soil is sifted in a layer of about one millimeter thickness upon glazed paper, on a wooden table, and placed in a small water-tight covered box, twelve by nine by eight inches, in which there is about an inch of water; the interior sides and cover of the box should be lined with blotting paper, kept saturated with water, to insure the saturation of the air.

Air-dried soil yields results varying from day to day to the extent of as much as thirty to fifty per cent, nor have we any corrective formula that would reduce such observations to absolute measure. Knop's law, that the absorption varies directly as the temperature, while applicable to low percentages of saturation, is wide of the truth when saturation is approached. The ordinary temperature of cellars will serve well in these determinations without material correction.

After from eight to twelve hours the earth is transferred as quickly as possible, in the cellar, to a weighed drying tube and weighed. The tube is then placed in a paraffin bath; the temperature gradually raised to 200° and kept there from 20 to 30 minutes, a current of dry air passing continually through the tube. It is then weighed again and the loss in weight gives the weight of hygroscopic moisture from saturated air.

The reason for adopting 200° as the temperature for drying instead of 100° is that water will continue to come off from most soils at the latter temperature for an indefinite time, a week or more, before an approach to constancy of weight is attained; and that up to 200° only an arbitrary limit can be assigned for the expulsion of hygroscopic moisture. Moreover, the great majority of soils, especially those poor in humus, will reabsorb moisture from a saturated atmosphere to the full extent of that driven off at 200°.

313. Estimation of the Absorption Power of Soils for Aqueous Vapors.[21]—*Method A.*—The fine earth, from ten to 20 grams, is spread out on a surface of about 25 square centimeters, and left for several days. The temperature of the air and the loss of

[21] König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, 2nd edition, 1898 : 61.

weight are determined from time to time. This evaporation is continued until the weight remains practically constant. Afterwards by drying the sample at 100° the amount of hygroscopic moisture is determined. A similar result can be reached if the sample is first dried at 100°, or over sulfuric acid at ordinary temperatures, and then the increase in weight observed which the sample acquires on being exposed for several days to the atmosphere under ordinary conditions. Soils with about the same content of humus show variations in the power to absorb aqueous vapors which are almost proportional to the amount of clay which they contain. With the increase of humus substance, the power of the soil for absorbing moisture is increased, so that a sandy soil which is rich in humus often will retain as much moisture in an air-dried state as a clay soil which is poor in humus. If the experiment is carried on by drying over sulfuric acid instead of at 100°, the sample should be left from four to seven days in order that a constant weight may be reached. Even after this time the loss in weight is generally from 0.2 to 1.5 per cent less than when the sample is dried at 100°.

Method B.—In order to determine the amount of aqueous vapor which a soil will absorb in an atmosphere saturated with the vapor the following method is used:

The sample of air-dried soil in a flat dish of given surface *viz.*, about 20 grams of soil to 25 square centimeters surface, is placed in a vessel over water without contact with the water, and the whole of the apparatus is covered with a glass bell-jar. The sample is weighed at intervals of from six or eight hours until no appreciable increase of weight is observed. An empty vessel of the same size and character as that containing the soil is kept under the bell-jar, also in the same conditions, so that any increase in weight by the deposition of moisture on this vessel may be determined. This increase in weight is to be deducted from the total increase in weight of the vessel and the soil. Sandy and loamy soils become saturated in this manner in the course of the first 24 hours and remain after that unchanged in weight. Very clayey soils, and also those which are very rich in humus, require a much longer time, three or four days even. In this case it is better to

take a smaller sample of the soil; *viz.*, ten grams. The temperature of the air within the glass vessel, of course, must be taken into consideration.

Method C.—The same flat dish and the same quantity of soil as in the other methods are used in this determination. The sample is left out over night where it can be fully saturated with dew. The amount of dew which appears on the bushes should be noted and also the temperature of the air and the percentage of clouds in the sky. An experiment should also be made on spots of earth which are entirely free from vegetation in order that the difference in the amount of water absorbed in places practically devoid of dew and in places where the dew is abundant may be observed.

Method D.—Deeper flat dishes are used for this determination so that the depth of soil contained in them shall be from one to three, or even six centimeters. The sample of soil is completely air-dried and in a state of fine subdivision. The vessels containing the soil are placed in a locality saturated with aqueous vapor or in the open air during the night where they are subjected to the influence of the cooling of the atmosphere and the deposition of dew. Note is made of the different amounts of moisture absorbed by the layers of earth of different thicknesses in a given time. Observation is also made of the depth to which the moisture sinks in the sample of soil under consideration.

314. Estimation of the Absorption Power of the Soil for Oxygen and Atmospheric Air.[22]—From 50 to 100 grams of air-dried soil are placed in a glass vessel of about 500 cubic centimeters capacity, and the flask closed wtih a stopper after the addition of enough water to make the percentage of moisture in the soil about 20. After from eight to fourteen days the air contained in the vessel is analyzed for oxygen, nitrogen, and carbon dioxid, with special reference to the determination of how much oxygen has disappeared and how much the carbon dioxid has been increased. As an alternative method, 25 grams of the soil are moistened with tolerably concentrated potash lye in a small glass vessel, which is itself joined with air-tight connections to an

[22] König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, 2nd edition : 1898 : 63.

azotometer in which a known volume of air is confined by quicksilver. The glass vessel is frequently shaken during the progress of the experiment. From the diminution of the volume of air in the apparatus after from one to four days the quantity of oxygen absorbed is approximately calculated.

315. **General Method of Determining Absorption.**—A convenient method is as follows:[28] The soil, in a state of fine powder, is dried at from 100° to 105° to a constant weight. It is then placed in an absorption tube of the following construction:

The absorption tube consists of a U-shaped wide glass tube, both ends of which are supplied with small glass tubes sealed upon the end of the U-tube, and these are furnished with tightly-ground glass stop-cocks. Above these stop-cocks these small tubes are bent in opposite directions at right angles. On the bend of the U is sealed another tube which is furnished with a ground glass stopper. Through this opening the U-tube can be filled with the sample of soil. When the tube is filled, the glass stopper inserted, and the two stop-cocks on the small tubes closed, the contents of the tube are completely excluded from the external atmosphere. Many of these tubes can be used at once so as to hasten the progress of the work.

The tubes after filling are placed in a drying oven with the stop-cocks open. The stop-cocks are closed before the tubes are removed, placed in a desiccator for cooling preparatory to weighing. The weighed tubes are held in a tin box which can be placed in a water-bath which is kept at a given temperature by means of a thermostat. The top of the tin box is hinged and made of a thick non-conducting material so as to prevent any rapid change of temperature within. On the inner side of the box a small thin-walled glass tube is carried around four times. One end of this tube passes through an opening in the side of the box by means of which it can be connected with the gas apparatus outside. The other end of it is connected directly with the absorption tubes.

The absorption tubes are so connected among themselves that when ammonia or carbon dioxid is employed the gas passes

[28] von Dobeneck, Forschungen auf dem Gebiete der Agrikulturphysik, 1892, **15** : 163, et seq.

through one of the tubes before it can reach the next, and so on. For experiments with water gas, however, that is, air charged with aqueous vapor, the arrangement must be different. While in the case of ammonia and carbon dioxid the composition of the gas is not changed by passing through the samples of soil, the case is quite different when air charged with aqueous vapor passes through. In the latter case the amount of aqueous vapor in the air would be notably lessened in passing from sample to sample on account of the retention of a part of the aqueous vapor by the soil. In this case, therefore, the saturated air, after it has passed through the glass tube around the inside of the box in order to reach the proper temperature, is conducted into a receptacle of glass which has a number of connections equal to the number of absorption tubes so that the saturated air can pass directly into each one of them.

The gases which are to be used for the experiments are prepared in proper apparatus and are forced through the samples of soil, either by pressure as in the case of ammonia or carbon dioxid, or by means of aspirators as in the case of air saturated with aqueous vapor.

The carbon dioxid employed is purified by passing over sodium carbonate and calcium chlorid.

The ammonia is prepared by the action of finely powdered lime on ammonium chlorid, and is dried by passing over lime and sticks of potassium hydroxid.

The air which is to be saturated with aqueous vapor, in order to purify it from dust, carbon dioxid, and ammonia, is passed through two flasks in which are contained respectively, dilute sulfuric acid and potash lye. It is afterwards thoroughly saturated with aqueous vapor at the temperature desired.

Various kinds of soil material may be employed as follows:

(1) Pure quartz sand.—Freed from all fine particles by subjection to silt analysis, afterwards boiled with hydrochloric acid and washed with water to free it from all clayey materials. The sand prepared in this way is passed through different sieves in order to prepare it in different states of fineness.

(2) Quartz powder.—Prepared from pure quartz crystals by grinding.

(3) Kaolin.—Material such as is used in the manufacture of the finest porcelain which, after being freed of all foreign matter, is rubbed to a fine powder in a porcelain mortar.

(4) Humus.—Washed with ether and alcohol, boiled with hydrochloric acid, washed, dried, and reduced to a state of fine powder.

(5) Iron oxid.

(6) Calcium carbonate.—Precipitated, washed and dried.

(7) Soil mixtures.—Prepared artificially by mixing the kaolin, quartz, and humus, above mentioned.

The quantity of gas absorbed by each of these materials is determined by filling the tubes, as above mentioned, with the dried material. The content of each tube is previously determined by filling with mercury and weighing. Having determined the weight of the substance after the expulsion or calculation of the volume of the air contained within its pores, it is treated with the gas in the apparatus described above and weighed from time to time until no further increase of weight takes place.

The method of calculating the results is shown in the following scheme:

Let

P' = weight of the empty tube filled with air at 100°.

V = content of the absorption tube.

pl = weight of the air in the tube ($pl = V \times$ specific gravity of the air at 100°).

pt' = weight of the tube ($pt' = P' - pl$).

P^2 (second weighing) = weight of the tube filled with the substance with the included air at 100°.

v^s = volume of the substance calculated according to the formula

$$v^s = \frac{P^2 - P'}{s^s - \text{specific gravity of the air}}.$$

s^s = specific gravity of the substance.

vl = volume of the air in the flask filled with the substance ($vl = V - v^s$).

pl′ (weight of this included air) = vl × specific gravity.

p^s = weight of the substance ($p^s = p^s - pt' - pl$).

P^s = weight of the apparatus at the end of the experiment.

sg = specific gravity of the gas employed for saturation.

pg (weight of the gas remaining over the substance) = vl × sg.

pa (weight of the absorbed gas) = $P^s - pt' - p^s - pg$.

Then if p^s gram of substance absorbs pa gram of the gas, 100 grams of substance would absorb $\frac{100 \times pa}{p^s}$ grams.

The specific gravities of the gases employed are calculated from the tables given by Landolt and Börnstein in "Physical and Chemical Tables," page 5.

The specific gravity of the quartz sand employed was 2.639; of the quartz powder, 2.622; of the kaolin, 2.503; of the humus, 1.462; of the iron hydroxid, 3.728; and of the calcium carbonate, 2.678.

One liter of ammonia, at a pressure of 760 millimeters of mercury and a temperature of 0°, weighs 0.7616 gram; one liter of carbon dioxid, 1.9781 grams; one liter of aqueous vapor, 0.8064 gram and one liter of dried-air, 1.2931 grams.

At a pressure of 720 millimeters, and at 20° temperature, a liter of air saturated with aqueous vapor at 0° weighs 1.1383 grams; saturated at 8.6°, 1.1362 grams; saturated at 10°, 1.1358 grams; saturated at 14°, 1.1340 grams; saturated at 18.2°, 1.1330 grams; saturated at 20°, 1.1321 grams; saturated at 30°, 1.1313 grams.

The general results of the experiments are as follows:

ABSORPTION AT 0°.

	Aqueous vapor from saturated air.		Ammonia.		Carbon dioxid.	
	Grams.	Cubic centimeters.[1]	Grams.	Cubic centimeters.[1]	Grams.	Cubic centimeters.[1]
100 grams quartz....	0.159	197	0.107	145	0.023	12
100 " kaolin....	2.558	3,172	0.721	947	0.329	166
100 " humus ...	15.904	19,722	18.452	24,228	2.501	1,263
100 " $Fe_2(OH)_6$.	15.512	19,236	4.004	5,275	6.975	3,526
100 " $CaCO_3$....	0.224	278	0.256	320	0.028	14

[1] Reduced to 0° and 760 millimeters pressure mercury.

The foregoing methods will suffice to show the procedures to be

followed in estimating the maximum amount of any common gas or vapor a given quantity of soil may be made to absorb. We pass next to consider the quantities of gases or vapor soils *in situ* may hold.

316. **Method of Boussingault.**[24]—This method is the oldest and most simple procedure for estimating the nature of the gases held in a soil *in situ*.

For the purpose of collecting the sample of gas from the soil a hole from 30 to 40 centimeters in depth, is dug, and a tube placed in it in a vertical position, having on its lower extremity a bulb perforated with fine holes. The hole is filled and the earth closely packed around the tube which is left for 24 hours. At the end of that time the tube is slowly aspirated until a volume of gas approaching from five to ten liters is obtained.

Estimation of Carbon Dioxid.—The carbon dioxid in the sample of gas is estimated by allowing it to bubble through a solution of barium hydroxid.

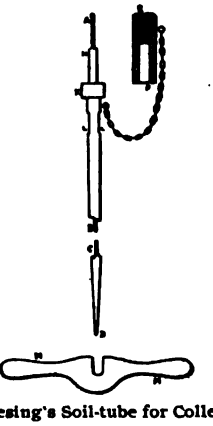


Fig. 73. Schloesing's Soil-tube for Collecting Gases.

Estimation of the Oxygen.—The oxygen is estimated in a separate sample of the gas by means of potassium pyrogallate.

The chief objection to this simple process is the uncertainty of being able to obtain an average sample of the occluded gas. In digging the hole and refilling, there must evidently be a considerable disturbance of the original distribution of the gas or vapor.

[24] Encylopédie chimique, 4 : 199.

No greater detail concerning these methods of the direct aspiration of the air is considered necessary inasmuch as the methods about to be described, while more elaborate, are superior in accuracy to the older methods mentioned. In general, in these experiments, it is deemed sufficient to determine the carbon dioxid only.

317. **Method of Schloesing.**—The apparatus used by Schlösing[25] in the collection of the soil gases consists of a steel tube (Fig. 73) a little over one meter in length, ten millimeters in external diameter, and one and one-half to two millimeters in internal diameter. The end which penetrates the soil is made slightly conical for a distance of from 25 to 30 centimeters. By reason of the shape of the tube, when it is driven into the soil all connection between the orifice in the point of the tube and the external air is prevented. The obstruction of the internal canal of the tube is prevented by introducing a thread of steel which penetrates the whole length of the tube. This thread, represented by A, B, C, D, is flush with the interior extremity of the tube at D. It extends for about three centimeters above the upper end of the tube in order to be easily handled when it is to be removed.

For the purpose of driving the tube into the soil its upper part is covered with a cylindrical piece of steel, EF, in the interior of which are freely engaged H and A. This head piece rests upon a ring of steel, K. This ring is fastened solidly into the tube. On striking the piece EF the tube and the steel wire in the center are driven together into the soil. The tube is flattened at L and L′ in order to be embraced by the key MM, the employment of which is necessary in order to revolve the tube around its axis when it is being driven into the soil. When the tube has been driven to the depth desired, the steel wire is withdrawn and it is immediately connected at H with the rubber tube N (Fig. 74) belonging to the system PQT and furnished with a pinch-cock X. The system PQT comprises the following elements: PQT made of a capillary glass tube in the form of a T. The lower end of the tube P is closed by the larger glass tube O, sealing the end of P wtih a little mercury. O is held to P by the cork S, which is attached firmly enough to prevent O from dropping off, but is furnished

[25] Annales de Chimie et de Physique, 1891, [6], **28** : 362, et seq.

with a canal in order to allow the air to flow in or out freely. This system is connected with the system UV by the rubber connection T. U is a glass vessel having the constrictions as indicated

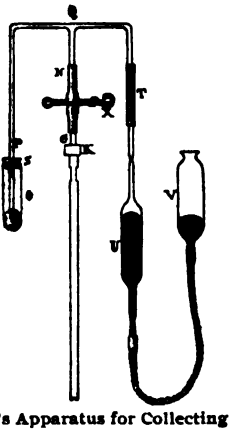


Fig. 74. Schloesing's Apparatus for Collecting Gases from Soil.

in its stem above and below the bulb. V is a glass vessel of convenient size connected with U by the rubber tubing as indicated. The capacity of the cylindrical portion of U should be from 15 to 18 cubic centimeters.

To get a sample of soil gas, F is lifted above U. The air is driven from U and escapes through O, which acts as a true valve. When the mercury has completely filled U the pinch-cock X is opened and V depressed gradually. The gas coming from the soil is thus collected in U. A few cubic centimeters of the soil gas are collected in this way, the pinch-cock X is again closed and V is raised in order to drive the whole of the contents of U again through O. In this way the whole of the air which the capillary vessel originally contained is removed and all parts of it remain filled with soil gas. Two or three operations, using from five to ten centimeters of soil gas in all, will be sufficient to completely free the apparatus from its original content of air. U is then entirely filled by depressing V, and it is then hermetically sealed at the two constricted points by means of an alcohol lamp. The sealed tube can then be transported to the laboratory and its contents subjected to eudiometric analysis.

Without displacing the tube from the soil, several samples of gas can be taken from the same spot. A sufficient number of the bulbs U should be at hand to hold the required number of samples. Instead of submitting the sample to eudiometric analysis it is usually sufficient to determine the quantity of carbon dioxid which it contains, inasmuch as numerous experiments have shown that in 100 parts of soil gas the oxygen and carbon dioxid together constitute 21 parts. No appreciable trace of marsh gas, or other combustible gas, has yet been detected in ordinary arable soils. These gases have only been found in special soils from marshes, in the neighborhood of gas wells, etc., and not in arable soils.

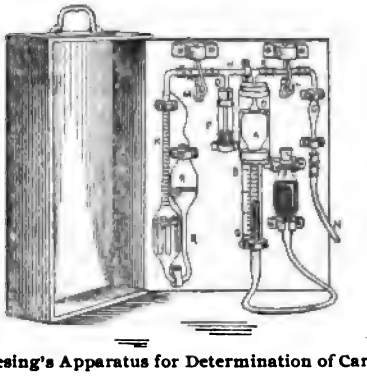


Fig. 75. Schloesing's Apparatus for Determination of Carbon Dioxid.

318. Apparatus for Estimating the Carbon Dioxid.—The apparatus used for determining the carbon dioxid in Schlösing's work consists of the apparatus shown in Fig. 75. A represents a glass vessel surrounded by a jacket of glass, full of water, and sealed on its lower part to the tube BC of about six millimeters internal diameter. On its upper part it is sealed to the capillary tube D. The tube BC is graduated from C in hundredths of the volume of DAC, which volume is about 12 cubic centimeters. On its lower part it is connected by a rubber tube with a reservoir F which is capable of being raised or lowered. GHK are capillary tubes connected together by the rubber tubes L and M, which are furnished with pinch-cocks. The tube G is connected to a vacuum by the rubber tube N. The rubber tube should be of very small

internal diameter and from 40 to 50 centimeters in length. To the tube H are sealed, at right angles, the branch D and another branch O. This last dips into a little mercury which the tube P contains. It serves as a valve, permitting the exit of the gases but not their entrance. The tube K carries some lines engraved on its inferior part and is sealed to the system of the two bulbs Q and R. The bulb Q contains a concentrated solution of potash. It carries a number of pieces of glass tubing for the purpose of increasing the surface of the potash solution.

All the parts of the apparatus are fixed upon a rectangular board, 19 centimeters broad by 20 centimeters long. This forms one of the faces of a wooden box to which it is hinged and which serves for the transportation of the apparatus in a vertical position. The graduation of the tube BC is recorded behind this tube upon a card fixed upon the board. By means of these two graduations, the height of the mercury in the tube BC is most easily read, even when the tube is not perfectly vertical. Each one of the pinch-cocks L, and M, on its upper part is fixed in a sort of guard which prevents it from being displaced laterally during the processes of the manipulation, thus avoiding all danger of breakage.

After the operation is finished a little air is sent into Q in such a manner as to sensibly lower the level of the solution of potash, and the upper extremity of R is closed with a rubber stopper. Afterwards, the apparatus can be transported without any danger of the potash becoming engaged in the tube K and reaching the measuring tank A.

To proceed to the analysis, a stake is driven into the soil to which all of the apparatus can be fixed. At the side of the stake the apparatus for taking the sample, already described, is driven into the soil and this apparatus is connected by the tube N with the apparatus for determining the carbon dioxid. The pinch-cocks L, and M being closed, F is lifted until the mercury which runs from it fills A and approaches D. During this time the air which the apparatus contains has been driven out through O. The tube NGD is freed from air by opening the pinch-cock L, lowering F and drawing into A the gas coming from the soil; after-

ward closing L and driving out the gas through O. After two or three rinsings of this kind, which employ altogether only ten to 12 cubic centimeters, the gas which is to be analyzed is sucked into A. For this purpose F is lowered until the mercury in the tube BC is very near C. The pinch-cock L is closed and M opened. The reservoir F is displaced little by little by pressing lightly against the rectangular board in order to give it greater firmness in such a way as to fix the level of the mercury exactly at C, and the line is noticed where the solution of potash in K stands. The gas contained in the apparatus is under a pressure, the difference of which from the external pressure is represented by the column of the potash solution between the mark just noticed and the level of the same solution in the bulb R. In order to absorb the carbon dioxid, F is lifted until the mercury stands between D and E. The gas thus passes from A into Q. It gives up immediately its carbon dioxid to the potash solution. It is then made to come again into A, and afterward a second time into Q, in order to free it from the last trace of dioxid. Finally it is made to return to A and F is kept at such a height that the potash solution maintains in the tube K the same level as at the commencement of the operation. The gas is then at the same pressure to which it was subjected before absorption. The level of the mercury is then read on BC. At the time the apparatus is used, the measuring tube A should be slightly moist. If it is not so, a small quantity of water should be introduced which is afterward rejected, but which leaves a sufficient quantity of moisture upon the internal walls of A. In this way the gas will always, before or after absorption of carbon dioxid, be saturated with vapor of water, and the figure read in the last place upon the tube BC represents the percentage of carbon dioxid in 100 parts of the gas extracted from the soil supposed to be saturated with vapor at the temperature of the experiment.

During the course of the analysis, the temperature of the measuring flask, which is amost entirely surrounded with water, does not vary sensibly, but in a series of experiments which are executed at different times, the temperature of the measuring apparatus, which is that of the ambient air, may change much. It may oscillate between 10° and 25°, and exceptionally between 0°

and 30°, whence there are notable variations in the tension of the vapor of the gas measured. If it should be desired to calculate to 100 parts of dry gas the observations made at 30° upon 100 parts of saturated gas, it would be necessary to increase the percentage of carbon dioxid by about $^1/_{25}$ of its value. It is noticed that with the apparatus described above, the gas upon which the estimation is really conducted comprises not only that which the measuring apparatus contains from E to C before the absorption of the carbon dioxid, but also the small quantity which remains in the capillary tube KME at the moment when closing the pinch-cock M, after the second rinsing, the gas from the soil is aspired into EAC. On the other hand, there is left in the same tube KME when the final reading is made, some gas which belongs to that which has been measured at the end. These two small gaseous portions which we consider in the tube KME to be sensibly equal, do not contain any carbon dioxid and may be left out of consideration. That is why the volume of the measuring apparatus is limited to E and the graduation of the tube BC is in hundredths of the volume comprised from E to C. In reality the two portions are not absolutely equal because the two successive levels of the potash solution, which limit them in the tube K, are not absolutely identical. These two levels can differ in such a manner as to correspond to a volume of about $^1/_{1000}$ of the measuring apparatus. Thus the estimation is really made upon a volume of gas which may be greater or less by $^1/_{1000}$ than the volume of EAC; whence there might result an error of $^1/_{1000}$ in the estimation of the carbon dioxid, an error which is wholly negligible.

As a result of numerous analyses it is concluded, first, that the oxygen exists normally in the atmosphere of soils in large proportion; second, very probably the gaseous atmosphere of arable soils, to a depth of 60 centimeters, contains scarcely one per cent of carbon dioxid and about 20 per cent of oxygen; third, the highest percentages of carbon dioxid correspond to epochs of highest temperature and periods of greatest calm; fourth, the proportion of carbon dioxid increases ordinarily with the depth at which the samples are taken. This disposition of the carbon dioxid is not surprising, since near the surface the internal atmosphere is almost constantly diluted by external air by virtue of diffusion.

Fifth, from one epoch to another the composition of the atmosphere of the soil can undergo considerable variation.

319. **Determination of Diffusion of Carbon Dioxid in Soil.**—The method proposed by Hannén[26] is a convenient one to use in studying the rate of diffusion of carbon dioxid in soils. A large Woulff's bottle with three necks serves for the reception of the gas. The two smaller outer necks of the bottle carry two glass tubes bent outwards and provided with stop-cocks. One of these passes to near the bottom of the bottle and the other just through the stopper. The middle tubule of the bottle is of a size to give in section an area of about 22 square centimeters. It is made with a heavy rim two centimeters wide and plane ground. This rim carries a plane-ground glass plate with a circular perforation in one-half of it, of the size of the opening in the central tubule of the bottle. A glass cylinder, carrying a fine wire-gauze diaphragm near the lower end, fits with a ground-glass edge air-tight, over this aperture, being held in position by a brass clamp. The ground-glass plate moves air-tight between the cylinder and the bottle, so that the cylinder can be brought into connection with the bottle or cut off therefrom without in any way opening the bottle to the air. The plate and all ground movable surfaces should be well lubricated with vaseline.

The experiment is carried on as follows: The glass cylinder is filled with the soil to be tested, closed above with a rubber stopper carrying a gas tube, and then by moving the perforated glass plate brought into connection with the bottle. The side tube, with short arm inside the bottle, is then closed, and carbon dioxid introduced through the other lateral tube until the gas passing from the tube at the top of the cylinder is pure carbon dioxid.

The lateral tube is then closed and the bottle is placed in a water-bath and kept at a constant temperature of 20°. When the temperature within and without the apparatus is the same the reading of the barometer is made, the stopper removed from the top of the cylinder, and the process of diffusion allowed to begin. After from six to ten hours the glass plate is moved so as

[26] Forschungen auf dem Gebiete der Agrikulturphysik, 1892, **15** : 8, et seq.

to break the connection between the cylinder and bottle. The carbon dioxid remaining in the bottle is driven out by a stream of dry, pure air. The air is allowed to pass through the apparatus for about ten hours. The carbon dioxid driven out is collected in an absorption apparatus and weighed. The absorption apparatus should consist of a series of Geissler potash absorption bulbs and finally a U form soda-lime tube. In front of the absorption apparatus is placed a drying bulb containing sulfuric acid. Inasmuch as the temperature and pressure can be readily determined, the weight of carbon dioxid obtained is easily calculated to volume.

The weight of 1,000 cubic centimeters of carbon dioxid at 0° and 760 millimeters pressure is 1.96503 grams. Therefore one milligram is equivalent to 0.5089 cubic centimeter of the gas. The volume of the bottle should be carefully determined by calibration with water. The results should be calculated to cubic centimeters per square centimeter of exposed surface in ten hours. The depth of the soil layer is conveniently taken at 20 centimeters.

320. Statement of Results.—

THE SOIL PACKED LOOSELY IN THE DIFFUSION TUBE.
DIFFUSION TIME, TEN HOURS.

Diameter of soil particles. mm.	Weight of soil taken. Grams.	Pure carbon dioxid at beginning of experiment. cc.	Carbon dioxid at end of experiment. cc.	Cubic centimeters of carbon dioxid diffused for each square centimeter.
0.01 –0.071	520	2549.4	1230.3	59.9
0.071–0.114	550	2545.9	1269.2	58.0
0.114–0.171	590	2556.4	1354.2	54.6
0.171–0.250	620	2538.9	1336.1	54.6
0.250–0.500	660	2532.0	1374.5	52.6
0.500–1.000	680	2528.2	1440.2	49.5
1.000–2.000	690	2496.6	1396.9	50.0
Mixture of the above	720	2514.3	1572.5	42.8

In greater detail the calculation and statement of the results may be illustrated by the following data:

In the first experiment given in the above table the diameter of the soil particles varied from 0.010 to 0.071 millimeter. The weight of soil in the diffusion tube was 520 grams. The volume of gas, at 0° and 760 millimeters, before the diffusion began was 2549.4 cubic centimeters. The volume of carbon dioxid under

standard conditions remaining after ten hours of diffusion was 1230.3 cubic centimeters. This volume is calculated from the weight of carbon dioxid obtained in the potash bulbs, each milligram being equal to 0.5089 cubic centimeter of carbon dioxid. The volume of carbon dioxid diffused is therefore 2549.4 — 1230.3 = 1319.1 cubic centimeters. The per cent of carbon dioxid diffused is 1319.1 ÷ 2549.4 = 51.74. The volume of carbon dioxid diffused for each square centimeter of cross section of the diffusion tube is 1319.1 ÷ 22 = 59.9 cubic centimeters.

The carbon dioxid should be passed long enough to secure complete expulsion of the air before the determination is commenced.

321. **General Conclusions.**—The general results of the experiments with the diffusion apparatus to determine the effect of the physical condition of the soil upon the rate of diffusion are as follows:

1. The diffusion of carbon dioxid through the soil is, at a constant temperature, chiefly dependent upon the pores in the cross section of the column of soil. Therefore, the absolute quantity of the diffused gas is greater the larger the total volume of the pores and *vice versa.*

2. Every diminution of the volume of the pores, whether secured by pressure of the soil or by an increase in the moisture thereof, is followed by a decrease in the volume of diffused gas. The giving up of the carbon dioxid present in the soil atmosphere to the upper atmosphere by the method of diffusion is therefore the less the finer the soil is, the more compressed the soil particles are, and the larger the water content of the sample and *vice versa.*

3. The quantity of diffused carbon dioxid is diminished according to the measure of compression to which the soil is subjected but is not strictly proportional to the height of the soil layer.

4. In soils in which rain water percolates slowly the diffusion of the carbon dioxid on account of this property is depressed to a greater or less extent.

PART SIXTH

THE CHEMICAL ANALYSIS OF SOILS

322. **Preliminary Considerations.**—The sample of soil intended for chemical analysis should consist of the fine earth which has passed at least a one-millimeter mesh sieve and subsequently been completely air-dried. The time required for the air-drying of a soil varies with the nature of the soil, the temperature and the quantity of aqueous vapor in the air. Sandy soils dry rapidly and those containing large quantities of humus slowly. A high temperature accelerates and a humid atmosphere retards the process. Under the usual conditions and when the soil is exposed in thin layers, the drying should continue for about four days for an ordinary arable soil, and about six days for one very rich in organic matter. With peat and vegetable soils ten or 12 days with frequent stirring, even when in thin layers, are necessary to attain approximately a constant weight.

The soil is conveniently spread on a zinc or other metal sheet of sufficient area so that the layer will be only one or two centimeters in thickness. The weight before and after desiccation will give the percentage of moisture lost on air-drying, which, of course, will depend chiefly on the degree of saturation of the sample when taken and the atmospheric conditions prevailing during drying.

If samples of soil are got in very dry times it is often necessary to moisten them with distilled water in order to prepare them properly for air-drying.

The quantity of hygroscopic water which the sample loses at 100°-105° should be determined, and all subsequent calculations of the percentages of the various constituents be based on the water-free material. When a soil which has been dried at 100°-105° to a constant weight is heated to 140°-150° it loses additional weight not due necessarily to loss of water of constitution. A part of this loss may be due to hygroscopic moisture which is not given off at 100°-105°, and a part may be hydrocarbons, or other easily

volatile or decomposable organic or inorganic bodies. Before estimating the total loss on ignition it is recommended by most chemists to dry at 140°-150°. The samples of soil, however, intended for chemical examination should never be dried beyond the point which is reached by exposure in thin layers at ordinary room temperatures. The state of aggregation, degree of solubility, and general properties of a soil, may be so changed by absolute desiccation as to render the subsequent results of chemical investigation somewhat misleading. In the methods which follow the actual processes employed have been given, which in some instances transgress the general principle stated above, but in all cases standard and approved methods are given in detail, even if some of their provisions seem unnecessary or imperfect.

323. **Order of Examination.**—First of all in a chemical study of the soil should be determined, its reaction (with litmus), its water-holding power in the air-dried state (hygroscopicity), its content of combined water (hydrous silicates of alumina), its organic matter (humus and organic nitrogen), its content of carbon dioxid (carbonates of the alkaline earths), and the part of it soluble in strong acids. A determination of these values gives the analyst a general view of the type of soil with which he is engaged, and leads him to adopt such a method of more extended analysis as the circumstances of the case may demand.

For this reason those operations which relate to the above determinations are placed first in the processes to be performed, while the estimation of the more particular ingredients of the soil is left for subsequent description.

Next follows a description of the standard methods of estimating the more important elements passing into solution on treatment of a soil sample with an acid. The method of treating the insoluble residue, and the detection and estimation of rare or unimportant soil constituents, closes the analytical study of the soils.

With respect to the determination of nitrogen as nitric or nitrous acid in the soil and drainage waters, it has been thought proper to collect all standard methods relating particularly thereto into one group, and since these compounds are more nearly re-

lated to fertilizing materials they will only be noticed briefly in this volume and be given in full in the next.

The question of the practical utility of chemical soil analysis is one which has been the subject of much discussion. There is, of course, no question of its scientific value in connecting the soil with the rocks whose decay has furnished the principal part of its mass and in disclosing the total quantity of plant foods which it contains. A review of the various opinions entertained on this subject finds no proper place in a work of this character. Unless, however, intelligent soil analysis be productive of some good it would be a thankless task to collect and arrange the details of the processes employed. An accurate determination of the constituents of a soil may not always enable the chemist to recommend a proper course of treatment, but it will help in many ways to develop a rational soil diagnosis which will permit the physician in charge of the case, who last of all is the farmer, to follow a rational treatment which in the end will be productive of good.

The analyst will find in the methods given all that are approved by bodies of official or affiliated chemists, or by individual experience, and among them some method or methods which, it is hoped, will be suited, in the light of our present knowledge, to each case which may arise.

324. Reaction of the Soil.—In soils rich in decaying vegetable matter the excess of acid is often great enough to produce a distinct acid reaction.

On the contrary, in arid regions the accumulation of salts near the surface may produce the opposite effect.

In calcareous soils the excess of carbonate of lime is sufficient to maintain at all times at least a neutral state.

The causes of soil acidity, or rather of that condition of the soil which is corrected by lime, are not well understood.

The reaction of the soil is determined with a large number of indicators among which, for convenience and reliability, sensitive litmus paper, both red and blue, stands in the front rank. A sample of the soil, from 15 to 30 grams, is mixed with water to a paste and allowed to settle. The litmus paper is then dipped into the supernatant liquid. When the soil is very moist the lit-

mus paper is applied directly to its cut surface. Detailed methods of quantitatively determining the acidity of soils are given further on.

325. Determination of Water in Soil.—The following problems are presented:

(a) *The Determination of Water in Fresh Samples taken in Situ*—The content of water in this case varies with the date and amount of rain-fall, the capacity of the soil for holding water, the temperature and degree of saturation of the atmosphere, and many other conditions, all of which should be noted at the time the samples are secured.

(b) *The Determination of Water in Air-Dried Samples.*—In this case the soil is allowed to remain in thin layers, and exposed to the air until it ceases to lose weight. The quantity of water left is dependent on the capacity of the soil to hold hygroscopic water and to the temperature and degree of saturation of the air.

(c) *The Determination of the Total Water by Ignition.*—This process not only gives the free and hygroscopic moisture, but also combined water present in the hydrous silicates and otherwise. The estimation is complicated by the presence of carbonates and organic matter.

326. Determination of Water in Fresh Samples.—This determination requires that the sample, when taken from the field, should be so secured as to be weighed before any loss of moisture can take place. For this purpose it can be sealed up in tubes or bottles and preserved for examination in the laboratory.

The prime importance of water to plant growth renders of importance those processes which give accurate information respecting the water content of a soil and the relations of the water so contained to the needs of the plant. The actual percentage of water in a soil is always to be correlated with the properties of a soil for holding moisture. A sandy soil for example may furnish a growing plant with the necessary water long after its percentage content of moisture falls below the limit for a clay soil to sustain the same plant.

The samples are secured as described in paragraph 75. The locality and date are written on a label attached to the tube. The

tube holds from 60 to 70 grams of soil, and the moisture determination is made on this in the laboratory in the usual way.

It is desirable to have this sample represent a depth of from six to nine inches, thus rejecting the surface three inches, which are more liable to sudden and accidental changes.

327. **Method of Berthelot and Andre.**—The estimation of the water according to Berthelot and André[27] should be made under three forms; *viz.*,

1. Water eliminated spontaneously at ordinary temperatures.
2. Water eliminated by drying to constant weight at 110°.
3. Water eliminated at a red heat.

The water may be determined directly on a sample weighed at the time of taking and afterwards dried in the open air, and finally, if necessary, in a desiccator. For general purposes a sample of 100 grams, for exact work ten grams is exposed to the air. The dish in which the drying takes place is shallow, and during the time the sample is frequently stirred and thoroughly pulverized with a spatula which is weighed with the dish. The drying in the air is continued several days. The data obtained are not constant since they depend on the temperature and the degree of saturation of the air with aqueous vapor. The variations due to these causes, however, are not very wide. The process may be regarded as practically finished when successive weights sensibly constant are obtained. In this state the soils contain very little water eliminable at 110°. Drying in a desiccator over sulfuric acid presents few advantages over the process just described.

328. **Drying in a Desiccator.**—The sample dried as indicated above by the method of Berthelot and André is placed in a desiccator over sulfuric acid. It is better to have the sample traversed by a current of perfectly dry air, and in this case it should be placed in a tube, which is closed while weighing, to prevent absorption of moisture. Much time is also required for this operation, and it does not possess the practical value of the method of drying in the free air.

329. **Water Set Free at 110°.**—This is determined by Berthelot and André on a weight of from five to ten grams of soil. The

[27] Annales de Chimie et de Physique, 1892, [6], **25** : 292, et seq.

sample which has been employed for the preceding determination may be used. While this is going on in an air-bath heated at 110°, about ten times as much soil should be dried for the same time at the same temperature, and this should be preserved in a well-stoppered flask. All subsequent determinations are to be made with the soil dried at 110°.

The loss of weight in a soil increases with the temperature to which it is exposed. The apparent quantity of water, therefore, determined at 140° or 180° is always greater than that obtained at 110°. But when the temperature exceeds 110° there is danger of decomposing organic bodies with the loss of a part of their constituent elements. Carbon dioxid and ammonia may also be lost, as well as other volatile bodies.

330. **Estimation of Water Remaining After Air-Drying.**—The sifted sample is placed in quantities of five or ten grams in a flat-bottom dish and dried at 110° to constant weight. Finally the sample is incinerated, thus obtaining the water of constitution along with organic matter and carbon dioxid in carbonates. This treatment not only removes the moisture, but all other matters volatile at that temperature.

Petermann,[28] advises drying the sample to constant weight at 150°.

It is further recommended by Petermann to determine total volatile and combustible matters by igniting to incipient redness, allowing to cool, moistening with distilled water, and drying at 150°. In thus expelling both water of constitution and organic matter and restoring the water of constitution by subsequent moistening, it is claimed that a near approach to the real quantity of organic matter is secured. If all the water of constitution is restored this is doubtless true. The possibility of so changing the nature of the colloidal particles by ignition as to prevent them from reabsorbing the original content of water must be taken into consideration. There is little danger of decomposing carbonates by heating to incipient redness for a short time.

The analytical processes followed by the German Agricultural

[28] L'Analyse du Sol, Brussels, 1891 : 14.

Chemists[29] are performed on air-dry soils, except as noted below and the results calculated to the weight of soil dried at 100°. In determining loss on ignition, however, the preliminary drying is made at 140°, with the exception of peaty samples where so high a temperature is not admissible.

The Official Agricultural Chemists[30] advise to place five grams of air-dry soil in a flat-bottom and tared platinum dish; heat in an air-bath to 110° for eight hours; cool in a desiccator, and weigh; repeat the heating, cooling, and weighing, at intervals of an hour till constant weight is found, and estimate the hygroscopic moisture by the loss of weight, ascertained rapidly to avoid absorption of moisture from the air.

In the method described by König,[31] from ten to 20 grams of the fine earth, properly prepared by air-drying and sifting, for analysis, are heated at 100° to constant weight. For control, five grams are placed in a desiccator over sulfuric acid for two or three days.

The total loss on ignition is made at a low red heat after previous drying at 140°. The sample is then treated with ammonium carbonate solution, evaporated on the water-bath, gently ignited and the operation repeated until constant weight is obtained. This is done to restore any possible loss from the decomposition of carbonates, which as seen above, Petermann does not fear. On the other hand, if large quantities of ferrous oxid be present, it is converted into ferric oxid during ignition and the apparent loss in weight be less than really takes place.

Wolff directs that a small portion of the well-mixed earth, for example, 20 grams, be spread out on a flat zinc plate, and its changes in weight observed through several days. These observations are continued until the variations are so slight that the loss can be determined with sufficient exactness from the last weighings. The soil is then dried at 125° in a hot air-chamber. The loss in weight will give the mean hygroscopic moisture in the soil under the conditions in which the experiment is made.

[29] Die landwirtschaftlichen Versuchs-Stationen, 1891, **88** : 311.

[30] Bulletin 46, Bureau of Chemistry : 71.

[31] König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, second edition, 1898 : 15.

331. **Loss on Ignition.**—The loss on ignition represents any hygroscopic moisture not removed by previous drying, all water in combination with mineral matters as water of constitution, all organic acids and ammoniacal compounds, all organic matter when the ignition is continued until the carbon is burned away, all or nearly all of the carbon dioxid present in carbonates, when the ignition is long continued at a high temperature, and, finally, some of the chlorids of the alkalies, if the temperature have been carried too high or been continued too long.

The loss of carbon dioxid in carbonates may be mostly restored by moistening the ignited mass two or three times with ammonium carbonate, followed by gentle ignition for a few minutes to incipient redness, to remove excess of the reagent. The apportionment of the rest of the loss justly among the remaining volatile constituents of the original sample is a matter of some difficulty but may be approximately effected by the methods to be submitted.

332. **Determination of Loss on Ignition.**—*Method of the Official Agricultural Chemists.*[32] The platinum dish and five grams of soil used to determine the hygroscopic moisture may be employed to determine the volatile matter. Heat the dish and dry soil to low redness. The heating should be prolonged till all organic material is burned away, but below the temperature at which alkaline chlorids volatilize. Moisten the cold mass with a few drops of a saturated solution of ammonium carbonate, dry, and heat to 150° to expel excess of ammonia. The loss in weight of the sample represents organic matter, water of combination, salts of ammonia, etc.

According to Knop[33] the total loss on ignition is determined as follows: About two grams of the fine earth are carefully ignited until all organic matter is consumed. The sample is then mixed with an equal volume of finely powdered, pure oxalic acid, and again heated until all the oxalic acid is melted and finally decomposed. After coling, the sample is weighed, again mixed with

[32] Bulletin 46, Bureau of Chemistry, 72.

[33] König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, 2nd edition, 1898 : 15.

half as much oxalic acid as before, ignited, cooled, weighed, and the process continued until the weight is constant.

The method recommended by König consists in igniting about ten grams of the fine earth at the lowest possible temperature until all the humus is destroyed. Thereafter the sample is repeatedly moistened with a solution of ammonium carbonate and ignited after drying at 100°, until constant weight is obtained. In soils rich in carbonates some carbon dioxid may be lost by the above process. For this a proper correction can be made by estimating the carbon dioxid in the sample, both before and after the execution of the above described process.

The method described by Frühling as much used in the German laboratories, consists in igniting ten grams of the fine earth, previously dried at 140° in a crucible placed obliquely on its support and with the cover so adjusted over its mouth as to give a draft within the body of the crucible. The ignition, at a gentle heat is continued until on stirring with a platinum wire no evidence of unconsumed carbon is found. The moistening with solution of ammonium carbonate, should not take place until the contents of the crucible are cool. Subsequent ignition, at a low heat for a short time, will remove the excess of ammonium salt.

333. **Method of Berthelot and André.**[34]—The earth dried at 110° contains still a greater or less quantity of combined water. The water united with alumina, silica and certain salts is meant, but not the water of constitution belonging to organic bodies. The exact estimation of this water offers many difficulties. The total loss obtained at a red heat embraces:

(1) The water combined with zeolitic silicates, with alumina and with organic compounds:

(2) The water produced by the combustion of the organic compounds:

(3) The carbon dioxid resulting from the partial decomposition of the calcium and magnesium carbonates:

(4) The carbon burned and the nitrogen lost during ignition. The measure of the loss of weight in an earth heated to redness

[34] Annales de Chimie et de Physique, 1892, [6], **25** : 289, et seq.

in contact with the air is not therefore, an exact process of estimating water or even volatile matters.

A better defined result is obtained in carefully burning a known weight of earth either in a current of free oxygen, or with lead chromate. The water produced in such a combustion is secured in a U-tube filled with pumice stone saturated with sulfuric acid, the carbon dioxid being absorbed afterwards in potash bulbs and by solid potash. The weight of earth burned is chosen so as to furnish a convenient weight of both water and carbon dioxid. In general about five grams are sufficient. When the combustion is made with oxygen, the soil is contained in a boat and the products of the combustion are carried over a long column of copper oxid heated to redness. The residue left in the boat is weighed at the end of the operation, and in this residue it is advisable to determine any undecomposed carbonate. Should the sample burn badly and be mixed with carbonaceous matter at the end of the operation, it will be necessary to substitute the lead chromate method. In this case, of course, the residue left after combustion is not weighed. Whichever method is employed gives a quantity of water originally combined with the soil, plus the quantity arising from the combustion of the hydrogen of the organic matter. The details of the processes for organic combustion will be given in a subsequent part of this manual. It is not possible to divide the water between these two sources directly, but this can be done by calculation, which gives results lying within the limits of probability. The method follows:

The organic nitrogen, determined separately, by soda-lime, the method of Kjeldahl, or volumetrically, is derived from proteid principles resembling albuminoids containing about 16% of nitrogen. The nitrates contained in the earth are in such feeble proportion, as to be negligible in this calculation. The total weight of these nitrogenous principles in the soil is therefore easily calculated. The carbon contained in the proteids is then calculated on a basis of 53 per cent of their total weight, and the hydrogen on a basis of 7.2 per cent. From the weight of the total organic carbon (determined as described further on) is subtracted the carbon present in the proteids. The remainder corresponds to the

organic carbon present as carbon hydrates, (ligneous principles containing 44.4 per cent carbon and 6.2 per cent hydrogen). By adding together the weight of the hydrogen contained in the ligneous principles, and the hydrogen contained in the proteids, and multiplying the sum by nine, the weight of water formed by the combustion of all the organic matter in the sample is obtained. This is subtracted from the weight of the total water obtained by direct determination as described above. The difference represents the weight of water combined with the minerals, etc., as well as with organic matters.

334. **Method of van Bemmelén.**[35]—According to the view of van Bemmelén, the soil contains colloidal humus and colloidal silicate, which complicate the determination of water. The colloids retain water in varying quantities, depending upon the following conditions:

(1) Upon their composition and state of molecular equilibrium.

(2) Upon the pressure of the aqueous vapor.

(3) Upon the temperature.

At each degree of temperature, the quantity of absorbed water which a colloid can retain in a space saturated with aqueous vapor, is different. The quantity of water which air-dried earth gives off at 100°, has therefore, no special significance unless all conditions are known.

In addition to the estimation of the quantity of water which soils, in their natural condition, are capable of taking up and holding, at ordinary temperatures, the estimation of the quantity of water which they can take up in different temperatures in spaces saturated with aqueous vapor should be of interest. It follows, therefore, that there is no special value in data obtained by drying earth at 100° or 110°. For the purpose of comparison, it is preferable to select that point at which the soil is dried over sulfuric acid, the point at which the tension of the water vapor in the soil, at a temperature near 15°, approaches zero. The water which still remains in the soil under these conditions is characterized as firmly combined water.

[35] Die landwirtschaftlichen Versuchs-Stationen, 1891, **38** : 279, et seq.

Van Bemmelén truly observes that only in soils which contain no carbonates and no chlorids and sulfids, can the loss on ignition be regarded as the sum of the humus and water content. By moistening with ammonium carbonate, the correction for expelled carbon dioxid cannot be correctly made as has been supposed up to the presenet time. In the first place, ignited magnesia, when it has lost its carbon dioxid, does not take this up completely on moistening with ammonium carbonate; in the second place, reactions with the chlorids may take place; and in the third place, the lime which is in the humus will be converted into calcium carbonate. Chlorids on ignition may be volatilized or oxidized. The sulfuric acid formed from the sulfids, on ignition, can expel carbon dioxid; further than this the iron of pyrites takes up oxygen on ignition. All these influences make the numbers obtained from loss on ignition extremely variable.

With sea slime van Bemmelén has weighed the soil after the elementary analysis and estimated, in addition to the carbon dioxid, both chlorin and sulfuric acid therein. The comparison of these estimations with those of CO_2, Cl, SO_3 and S, made in the original soil, gave the necessary corrections; *viz.*, for the increase in the weight through oxidation of sulfur and iron, and for the decrease in weight through the volatilization of sodium chlorid, sulfur, and carbon dioxid. A trace of chlorin was evolved as ferric chlorid, nevertheless, the molecular weight of sodium chlorid, 58.5 is scarcely different from the equivalent quantity of ferric chlorid, ⅙ of 325 *viz.*, 54. For this reason the estimation of loss of water, on ignition, of sea slime is less exact than that of soils which are free from carbonates and sulfids and which, as is usually the case with tillable soils, contain only small quantities of chlorids and sulfates.

The Strongly Combined Water.—Water which, at a temperature of near 15°, in a dry atmosphere, still remains in the soil, is chiefly combined according to van Bemmelén with the colloidal bodies therein. Its estimation presents, naturally, difficulties and is not capable of any great exactness. The quantity of strongly combined water, on the one hand is determined from the difference between the loss on ignition and the quantity of humus pres-

ent, calculated from the content of carbon; and on the other hand, from the difference between the water obtained by elementary analysis and the water which corresponds to the calculated quantity of humus. If the hydrogen content of humus is correctly taken and no appreciable error is introducted through the factor 1.724, both of these differences must agree. On the other hand the hydrogen content of the humus can be computed from the difference between the water found and the calculated content of the firmly combined water.

The hydrogen content of humus bodies, dried at 100°, varies between four and five per cent. Eggertz has found the content from 4.3 to 6.6 per cent of hydrogen in 13 soils which he first treated with dilute hydrochloric acid then extracted with ammonia or potash lye and precipitated this alkaline extract with acid. The method of applying these principles to soil analysis is indicated in the following scheme:

A volcanic earth from Deli gave, on elementary analysis:

	Per cent.
Carbon	2.94
Water	14.78
Nitrogen	0.28
Loss on ignition	17.54

FIRST CALCULATION.

Loss on ignition	17.54
Humus = carbon, 2.94 × 1.724 =	5.07
Difference = firmly combined water	12.47

Assuming that a humus dried over sulfuric acid contains five per cent of hydrogen, the second calculation is made as follows.

SECOND CALCULATION.

5.07 humus × 5 per cent. = 0.253 per cent. of hydrogen in humus corresponding to 2.28 per cent. of water.

	Per cent.
Water found	14.79
Difference = firmly combined water	12.51

THIRD CALCULATION.

Firmly combined water	12.47
Water from the hydrogen in humus	2.28
Total water	14.75
Found	14.79

In this way, in three other volcanic earths and in an ordinary

alluvial clay from Rembang, there were found by analysis and by calculation the following percentages of water:

	1.	2.	3.	4.	5.
Percentage of water calculated..	14.75	7.74	8.06	4.90	6.01
" " " found.....	14.79	7.63	8.05	4.70	6.00

On the contrary, when the calculation is made from sea-slime taken from under the water a higher content of hydrogen must be assumed; *viz.*, about six per cent. In two samples of sea-slime calculated in this way the following numbers were obtained:

Percentage of water calculated	8.61	3.71
" " " found	8.53	3.57

It is, therefore, quite evident that the organic compounds of soil taken from under the sea-water are richer in hydrogen than those exposed to the air or in cultivation.

335. **Uniform Conditions of Desiccation.**—It is evident from the foregoing discussion that the exact determination of water in soils, in its various forms of combination, is a difficult analytical problem. Slight variations in temperature, or in forms of drying apparatus or in lengths of time the sample is submitted to desiccation or in the pressure of the air and its degree of saturation will influence more or less the final results. A general agreement among chemists in respect of all these details would at least lead to uniformity of results and possibility of comparison. Among many other valuable suggestions which have been made in this respect attention may be called to the observations of Puchner,[86] who points out the imperfections of some of the methods employed and prefers the electrical drying oven as more reliable when desiccation at 105° is desired.

336. **Determination of Moisture by Electrical Methods.**—The method proposed by Whitney for the estimation of water in the soil by electrical methods has been worked out by Briggs.[87]

This method is based on the principle that the resistance offered to the passage of an electrical current from one electrode to another when buried in the soil, varies with the amount of water in the soil. The electrical resistance is very nearly inversely proportional to the square of the water content expressed in percent-

[86] Die landwirtschaftlichen Versuchs-Stationen, 1901, **55** : 309.

[87] Division of Soils, Bulletin No. 15.

age of the weight of the soil. In these measuremnts it is necessary to maintain the temperature and the amount of salt in solution constant or to correct for their variations. The character of the salt solution must also be taken into account.

It is evident from a statement of the conditions of the problem that more time is required to determine the nature of the environment and to make the various determinations than would be required to ascertain the content of moisture by the usual drying process. Moreover, the standardization of the apparatus is secured by actual determinations of moisture by drying. Even granting the reliability of the process its practical application is not apparent. For the description of the instruments employed and the details of the manipulation, the original paper should be consulted.

337. **General Conclusions.**—In the foregoing paragraphs have been collected the most widely practiced methods of determining moisture in soil in both a free and combined state. The following conclusions may serve to guide the analyst who endeavors to determine the water in any or all of its conditions:

(1) The samples should be secured in such a way as to be representative of the actual moisture conditions and each sample be accompanied by recent meteorological data and the samples secured in great numbers over widely scattered areas. These samples should be dried at from 100° to 110° for rapid work, or where time can be spared may be air-dried.

(2) For a simple determination of the water left in the soil after air-drying (hygroscopic water) the method of the Association of Official Agricultural Chemists may be followed. There is much difference of opinion in respect of the proper temperature at which this moisture is to be determined. Much here depends on the nature of the soil. An almost purely mineral soil may safely be dried at 140° or 150°. A peaty soil, on the contrary, should not be exposed to a temperature above 100°. For general purposes the temperature chosen by the official chemists is to be recommended.

(3) Water of composition can only be determined by ignition. As has been fully shown, this process not only eliminates the water,

but also destroys organic matter, decomposes carbonates and sulfids, and, to some extent, chlorids. Subsequent repeated treatment with ammonium carbonate may restore the loss due to carbon dioxid, but in many cases not entirely. The water which comes from organic matter may be approximately calculated from the humus content of the sample, but as will be seen further on, the methods of estimating humus are only approximate. Nevertheless, in distributing the losses on ignition properly to the several compounds of the soil there is no better method now known than that of taking into consideration the humus content and carbonates present. The principles of procedure established by Berthelot and André, and van Bemmelén, are to be applied in all such cases, modified as cicumstances may arise according to the judgment of the analyst.

338. **Estimation of the Organic Matter of the Soil.**—The organic matter in the soil may be divided into two classes. First, the undecayed roots and other remains of plant and animal life, and the living organisms existing in the soil. The study of the organisms which are active in the condition of plant growth will be the subject of a special chapter. Second, the decayed or partially decayed remnants of organic matter in the soil known as humus. Such matter may be present in only minute traces, as in barren sand soils, or it may form the great mass of the soil under examination, as in the case of peat, slime, and vegetable mold. It is with the investigation of the second class of matter that the analyst has chiefly to do at present. The problems which are to be elucidated by the analytical study of such bodies are the following: (1) The total quantity of such matter in the soil. (2) The determination of the organic carbon and hydrogen therein. (3) The determination of total nitrogen. (4) The determination of the availability of the nitrogen for plant growth. (5) The estimation of the humic bodies (humus, humic acid, ulmic acid, etc.).

The importance of humus in the promotion of plant growth is sufficient excuse for the somewhat extended study of the principles which underlie the analytical methods, and the methods themselves, which follow.

339. **Total Quantity of Organic Matter.**—The total approximate quantity of organic matter in the soil can be determined by simple ignition, in the manner noted in the following paragraphs. When the proper correction for free and combined water is applied, and for carbonates and volatile chlorids, by the copper oxid or lead chromate combustion of the sample, the approximate total of the organic matter of all kinds is obtained.

340. **Estimation of the Organic Carbon.**—To estimate the organic carbon in a soil the sample may be burned in a current of oxygen, or after mixing with lead chromate.

In a Current of Oxygen.—When burned in a current of oxygen the sample is held in a boat and the gases arising from the combustion directed over copper oxid at a red heat. The carbon thus disappears as carbon dioxid and is absorbed and weighed in the usual way.

With Lead Chromate.—The lead chromate employed should be previously tested since it often contains other compounds, especially lead acetate and nitrate, furnishing in the one case both carbon dioxid and water, and in the other gaseous nitrogen compounds.

From two to ten grams of earth, according to its richness in organic matter, are used in the combustion. The total carbon dioxid is obtained in this process both from carbonates and organic bodies. The water and carbon dioxid are secured and weighed in the usual manner employed in ultimate organic analysis.

The oxygen method should be used in all cases possible. Although it does not always give the whole of the carbon dioxid present as carbonates, the rest can be easily estimated by treating the residue in the boat with hydrochloric acid, in an apparatus for estimating that gas.

Calculation of Results.—The whole of the carbon dioxid is determined either as has been indicated by direct combustion with lead chromate, or by taking the sum of the amounts by burning in a stream of oxygen and treating the residue in a carbon dioxid apparatus.

The carbon dioxid contained in the original carbonates should

be determined by direct treatment of the sample with acids in the usual way.

The carbon in organic compounds is determined by subtracting the carbon present as carbonates from the total.

From the organic carbon contained in the soil the humus is calculated on the supposition that it contains 58 per cent of carbon. It is, therefore, only necessary to multiply the percentage of carbon found by 1.724, or the carbon dioxid found by 0.471, to determine the quantity of humus in the dried soil.

341. Details of the Direct Estimation of Carbon in Soils by Various Methods.—(1) *Oxidation by Chromic Acid.*—The method of Wolff by oxidation with chromic acid has been worked out in detail by Warington and Peake.[38] It consists in treating the soil with sulfuric acid and potassium bichromate, or by preference with a mixture of sulfuric and chromic acids, the carbon dioxid evolved being estimated in the usual way. This method is recommended by Fresenius as an alternative to a combustion of the soil with copper oxid or lead chromate. It is apparently the method which has been most generally employed in agricultural investigations.

Ten grams of the finely powdered soil are placed in a flask of about 250 cubic centimeters capacity, provided with a caoutchouc stopper, through which pass two tubes, one for the supply of liquids, the other for the delivery of gas. The soil is treated with 20 cubic centimeters of water and 30 cubic centimeters of oil of vitriol, and the whole, after being thoroughly mixed, is heated for a short time in a water-bath, the object in view being the decomposition of any carbonates existing in the soil. Air is next drawn through the flask to remove any carbon dioxid which has been evolved. The stopper is next removed, and coarsely powdered potassium bichromate introduced. In the case of a soil containing three per cent of carbon, six grams of bichromate will be found sufficient, a portion remaining undissolved at the end of the experiment. The stopper is then replaced, its supply-tube closed by a clamp, and the delivery-tube connected with a series of absorbents contained in U-tubes. The first of these tubes contains solid

[38] Journal of the Chemical Society, London, 1880, **38** : 761 et seq.

calcium chlorid; the second, fragments of glass moistened with oil of vitriol; the third and fourth are nearly filled with soda-lime, a little calcium chlorid being placed on the top of the soda-lime at each extremity. The last named tubes are for the absorption of carbon dioxid, and have been previously weighed. The series is closed by a guard-tube containing soda-lime, with calcium chlorid at the two ends.

The flask containing the soil and bichromate is now gradually heated in a water-bath, the contents of the flask being from time to time mixed by agitation. A brisk reaction occurs, carbon dioxid being evolved in proportion as the soil is rich in organic matter. The temperature of the water-bath is slowly raised to boiling as the action becomes weaker, and is maintained at that point till all action ceases. As bubbles of gas are slowly evolved for some time, it has been usual in these experiments to prolong the digestion for four or five hours. When the operation is concluded the source of heat is removed, an aspirator is attached to the guard-tube at the end of the absorbent vessels, and air freed from carbon dioxid is drawn through the flask and through the whole series of U-tubes. The U-tubes filled with soda-lime are finally weighed, the increase in weight showing the amount of carbon dioxid produced. The object of the calcium chlorid placed on the surface of the soda-lime is to retain the water which is freely given up when the soda-lime absorbs carbon dioxid. The second U-tube filled with soda-lime does not gain in weight till the first is nearly saturated; it thus serves to indicate when the first tube requires refilling. The same tubes may be used several times in succession.

No increase in the carbon dioxid evolved is obtained by substituting chromic acid for potassium bichromate.

The organic matter of the soil appears to the eye to be completely destroyed by the digestion with sulfuric acid and potassium bichromate; the residue of soil remaining in the flask when washed with water is perfectly white, or the dark particles, if any, are found to be unaltered by ignition, and therefore to be inorganic in their nature. Under these circumstances considerable confidence has naturally been felt in this method. The complete destruction of the humic matter of the soil does not, however, nec-

essarily imply that the carbon has been entirely converted into carbon dioxid as has been pointed out by Wanklyn. According to his demonstration of the action of chromic acid on organic matter the oxidation frequently stops short of the production of carbon dioxid. While oxidation with chromic acid apparently leads to a complete reaction when the carbon is in the form of graphite, it would probably yield other products than carbon dioxid when the carbon exists as a carbohydrate. The doubt thus raised as to the correctness of the results yielded by the chromate method makes it desirable to check the work by the use of other methods for the determination of carbon. For this purpose Warington and Peake recommend:

(2) *Oxidation with Potassium Permanganate.*—In the trials with this method ten grams of soil are digested in a closed flask with crystals of potassium permanganate, and a measured quantity of solution of caustic potash containing five grams of potash for each 20 cubic centimeters. Seven grams of the permanganate are found to be sufficient for a soil containing 3.3 per cent of carbon. The flask is heated for half an hour in boiling water, and then for one hour in a salt-bath. The flask during this digestion is connected with a small receiver containing a little potash solution, to preserve an atmosphere free from carbon dioxid. Distillation to a limited extent is allowed during the digestion in the salt-bath.

The first part of the operation being completed a rubber stopper, carrying a delivery and supply-tube, is fitted to the flask, which is then connected with the system of U-tubes already described. Dilute sulfuric acid is then poured down the supply-tube, a water-bath surrounding the flask is brought to boiling, and maintained thus for one hour, after which air, free from carbon dioxid, is drawn through the apparatus, the U-tubes containing soda-lime being finally disconnected and weighed.

In the first stage of this method the carbon of the organic matter is converted into carbonate, and probably also into potassium oxalate.[39] In the second stage the oxalate is decomposed by the sulfuric acid and permanganate, and the carbon existing, both as

[39] Wanklyn, Philosophical Magazine, 1878, [5], 5 : 466.

oxalate and carbonate, is evolved as carbon dioxid, and absorbed by the weighed soda-lime tubes. Both F. Schulze and Wanklyn have employed potassium permanganate for the determination of organic carbon, but they have preferred to calculate the amount of carbon from the quantity of permanganate consumed, as, however, by so doing everything oxidizable by permanganate is reckoned as carbon, it seems better to make a direct determination of the carbon dioxid formed.

From the amount of carbon dioxid found, is to be subtracted that existing as carbonates in the soil, and in the solution of potash used. For this purpose an experiment is made with the same quantities of soil and potash previously employed, but without permanganate, and the carbon dioxid obtained is deducted from that yielded in the experiment with permanganate. If the potash used contains organic matter two blank experiments will be necessary, one with potash and permanganate, and one with soil alone.

A further difficulty arises from the presence of chlorids in the materials, which occasions an evolution of free chlorin when the permanganate solution is heated with sulfuric acid. This error occurs also with the chromic acid method, but in that case the quantity of chlorid is merely that contained in the soil, which is usually very small; in the permanganate method we have also the chlorid present in the caustic potash, and this is often considerable. Corrections for chlorin by blank experiments are unsatisfactory, the amount of chlorin which reaches the soda-lime tubes depending in part on the degree to which the calcium chlorid tube has become saturated with chlorin. It is better therefore to remove the chlorin in every experiment by the plan which Perkin has suggested, by inserting a tube containing silver foil, maintained at a low red heat, between the flask and the absorbent U-tubes.

The amount of carbon dioxid yielded by oxidation with potassium permanganate is found to be considerably in excess of that obtained by oxidation with chromic acids. To ascertain whether these higher results really represented the whole of the carbon present in the soil, trials were next made by actual combustion of the soil in oxygen.

(3) *Combustion in Oxygen.*—The most convenient mode of carrying out the combustion of soil is to place the sample in a platinum boat, and ignite it in a current of oxygen in a combustion tube partly filled with cupric oxid. A wide combustion tube is employed, about 20 inches long, and drawn out at one end; the front of the tube is filled for eight inches with coarse cupric oxid, the hind part is left empty to receive the platinum boat. The drawn out end of the combustion tube is connected with a series of absorbent U-tubes, quite similar to those employed for the estimation of carbon dioxid in the chromic acid method. Between these absorbent vessels and the combustion tube is placed a three-bulbed Geissler tube filled with oil of vitriol. The oil of vitriol is quite effective in retaining nitrous fumes. The wide end of the combustion tube is connected with a gas-holder of oxygen; the oxygen gas is made to pass through a U-tube of soda-lime before entering the combustion tube, to remove any possible contamination of carbon dioxid.

In starting a combustion the part of the combustion tube containing the cupric oxid is brought to a red heat, and oxygen is passed for some time through the apparatus. Ten grams of soil, previously dried, are placed in a large platinum boat, which is next introduced at the wide end of the combustion tube. The combustion is conducted in the usual manner, a current of oxygen being maintained throughout the whole operation. It is very useful to terminate the whole series of absorbent vessels with a glass tube dipping into water; the rate at which the gas is seen to bubble, serves as a guide to the supply of oxygen from the gas-holder, the consumption of oxygen varying, of course, with different soils, and at different stages of the combustion. At the close of the combustion, oxygen, or air freed from carbon dioxid, is passed for some time through the apparatus to drive all carbon dioxid into the absorbent vessels. One experiment can be followed by another as soon as the hind part of the combustion tube has cooled sufficiently to admit a second platinum boat. The same combustion tube can be employed for several days, if packed in the usual manner in asbestos.

The presence of carbonates in the soil occasions some difficulty in working the combustion method, as a part of this carbon dioxid

will, of course, be given up on ignition, and be reckoned as carbon. The simplest mode of meeting this difficulty is to expel the carbon dioxid belonging to the carbonates before the combustion commences. The method of Manning; namely, treatment with a strong solution of sulfurous acid, may be employed for this purpose. The ten grams of soil taken for combustion are placed in a flat-bottomed basin, covered with a thin layer of the solution of sulfurous acid, above mentioned, and frequently stirred. After a time the action is assisted by a gentle heat. When the carbonates have been completely decomposed the contents of the basin are evaporated to dryness on a water-bath; the dry mass is then pulverized, and removed to the platinum boat for combustion in oxygen. For the action of the sulfurous acid to be complete it is essential that the carbonates should be in very fine powder, since even chalk is but imperfectly attacked when present in coarse particles.

342. Comparison of Methods.—A considerable number of soils analyzed by the chromic acid method and by the combustion method, by Warington and Peake, with the assistance of Cathcart, show the following comparisons:

PERCENTAGE OF CARBON FOUND BY TWO METHODS IN SOILS DRIED AT 100°.

No.	Kind of soil.	Chromic acid method.			Combustion in oxygen method.			Per cent. yielded by chromic acid.
		Exp. 1.	Exp. 2.	Mean.	Exp. 1.	Exp. 2.	Mean.	
1.	Old pasture...	2.85	2.79	2.82	3.58	3.55	3.57	79.0
2.	" " ...	2.83	2.79	2.81	3.57	3.53	3.55	79.1
3.	" " ...	2.76	2.76	2.76	3.46	3.46	3.46	79.7
4.	" " ...	2.74	2.76	2.75	3.37	3.38	3.38	81.4
5.	" " ...	2.64	2.54	2.59	3.31	3.36	3.34	77.5
6.	" " ..	2.51	2.43	2.47	3.15	3.15	3.15	78.4
7.	" " ...	2.40	2.44	2.42	3.09	3.13	3.11	77.8
8.	New pasture..	1.92	1.93	1.93	2.41	2.40	2.41	80.1
9.	" " ..	1.66	1.81	1.74	2.39	2.43	3.41	72.2
10.	Arable soil....	1.78	1.78	1.78	2.14	2.13	2.14	83.2
11.	" "	1.21	1.14	1.18	1.40	1.43	1.42	83.1
12.	Subsoil	0.28	0.27	0.28	0.37	0.38	0.38	73.7

Of the above soils the arable soils, Nos. 10 and 11, were the only ones containing carbonates in any quantity exceeding a min-

ute trace. The two soils in question were treated with sulfurous acid before combustion, the others not.

All the determinations with chromic acid give distinctly lower results than on combustion in oxygen. Excluding analyses nine and 12, which were not made under the same conditions as the others, the relation of the carbon found by the two methods is tolerably constant, the average being 79.9 of carbon found by oxidation with chromic acid for 100 yielded by combustion in oxygen. The results obtained by the chromic acid method thus appear to be very considerably below the truth.

Four typical soils were analyzed by the permanganate, as well as by the chromic acid and combustion methods. The results obtained are as follows:

PERCENTAGE OF CARBON FOUND BY THREE METHODS IN SOILS DRIED AT 100°.

Kind of soil.	Combustion method. Mean. Per cent.	Chromic acid method. Mean. Per cent.	Permanganate method. Exp. 1. Per cent.	Permanganate method. Exp. 2. Per cent.	Permanganate method. Mean. Per cent.	Yielded by permanganate if carbon by combustion = 100. Per cent.
Old pasture.....	3.55	2.81	3.26	3.30	3.28	92.4
New pasture....	2.41	1.93	2.29	2.30	2.30	95.4
Arable soil	1.42	1.18	1.28	1.33	1.31	92.3
Subsoil.....	0.38	0.28	0.34	0.34	0.34	89.5

Oxidation by permanganate thus gives a much higher result than oxidation with chromic acid; but even the permanganate fails to convert the whole of the carbon into carbon dioxid, the product with permanganate being on an average of the four soils 92.4 per cent of that yielded by combustion in oxygen.

Wanklyn states that a temperature of 160°-180° is necessary in some cases to effect complete oxidation with permanganate and caustic potash. Such a temperature is found impracticable when dealing with soil, from the action of the potash on the silicates present; hence possibly the low results obtained.

Combustion in oxygen appears from these experiments to be the most satisfactory method for determining carbon in soil, nor is this method, on the whole, longer or more troublesome than the other methods investigated.

Warington and Peake have further determined the loss on ignition of the four soils mentioned above, with a view of comparing

this loss with the amount of organic matter calculated from the carbon actually present. In making this calculation they have taken as the amount of carbon in the soil, that found by combustion in oxygen, and have assumed with Schulze, Wolff, and Fresenius, that 58 per cent of carbon will be present in the organic matter of soils. The four soils were heated successively at 100°, 120°, and 150°, till they ceased to lose weight; the loss on ignition in each of these stages of dryness is shown in the following table:

PERCENTAGE LOSS ON IGNITION COMPARED WITH ORGANIC MATTER CALCULATED FROM CARBON.

Kind of soil.	Between 100° and ignition. Per cent.	Between 120° and ignition. Per cent.	Between 150° and ignition. Per cent.	Organic matter at 58 per cent. carbon. Per cent.
Old pasture	9.27	9.06	8.50	6.12
New pasture	7.07	6.88	6.55	4.16
Arable soil	5.95	5.70	5.61	2.44
Clay subsoil	5.82	5.39	4.76	0.65

The loss on ignition is seen to be in all cases very considerably in excess of the organic matter calculated from the carbon, even when the soil has been dried at as high a temperature as 150°. The error of the ignition method is least in soils rich in organic matter, as, for instance, the old pasture soil in the above table. The error reaches its maximum in the case of the clay subsoil, which contains very little carbonaceous matter, but is naturally rich in hydrated silicates, which part with their water only at a very high temperature.

The above methods of Warington and Peake have been given in detail, and in almost the verbiage of the authors for the reason that the working directions are clearly set forth, and may serve, therefore, as guides to the previous methods where only general indications of manipulation have been given.

343. **Modification of Cameron and Brazeale.**—In this method the combustion apparatus is arranged as shown in Fig. 76.[40]

The combustion is effected in a round-bottomed flask *F*, of about 400 cc. capacity, fitted with a three-hole rubber stopper. The stopper is fitted with a dropping funnel, a tube for the introduction of air previously freed from carbon dioxid by bub-

[40] Journal of the American Chemical Society, 1904, **26** : 29.

bling through a solution of potassium hydrate in the flask *G*, and a tube leading through a condenser to a train of absorption bulbs. This train contains, first, a Peligot tube *A*, containing a saturrated and slightly acidified solution of silver sulfate to absorb both hydrochloric acid and sulphur trioxid or dioxid should they be generated; then a guard tube *B*, containing concentrated sulfuric acid, followed by a potash bulb *C*, and an acid bulb *D*, to be weighed with the potash bulb. An acid guard bulb *E* completes the train. The whole apparatus is attached to an aspirator,

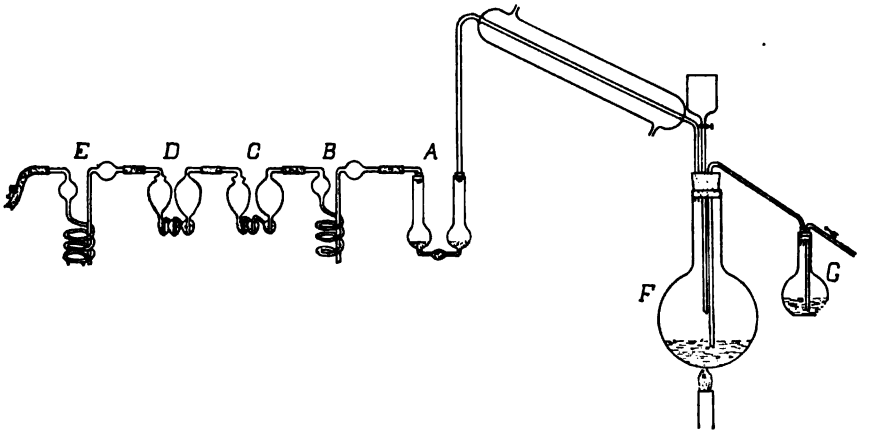


Fig. 76. Apparatus for determining organic matter by chromic acid method.

so that air free from carbon dioxid can be drawn through the combustion flask and train. The procedure is as follows:

A sample of the soil, usually about ten grams, is placed in the flask *F*. From five to ten grams of pulverized potassium bichromate are then added, and the whole mixed thoroughly by shaking, care being taken to prevent any of the mixture adhering to the sides of the flask above the level of the liquid. The flask is closed and a gentle stream of air drawn through the apparatus. After about ten minutes, concentrated sulfuric acid (sp. gr. about 1.83) is slowly and cautiously run in by means of the dropping funnel until the tip of the glass tube for the introduction of air is covered. When this point has been reached, and if no very vig-

orous action is taking place, the combustion flask is slowly heated until the sulfuric acid commences to give off fumes. It is held at this temperature for from five to ten minutes, and then allowed to cool slowly, unless there is reason to believe combustion has not been complete, in which case the temperature is again raised. During this time a current of air is kept passing through the apparatus. It is advisable to have the bulb of the dropping funnel empty before commencing the heating, so that the tube can be quickly opened, in case of danger of a sudden evolution of gas. In case the sample contain large amounts of chlorid, it is suggested that they be first heated with sulfuric acid until the chlorids are decomposed before the potassium chromate is added. If the potassium chromate be dissolved in the acid instead of being added in a powdered state to the soil the tendency to evolve chlorine appeared to be checked. No satisfactory reason for this is offered.

344. **Method of Messinger.**—In order to avoid the loss in carbon dioxid that attends the moist combustion of an organic body in chromic-sulfuric acid, Messinger has suggested the interposition of a short combustion tube between the flask where the decomposition takes place and the absorbing system where the carbon dioxid is collected.[41]

The process is based on the assumption the gaseous carbon compounds arising during the moist combustion are not composed exclusively of carbon dioxid, but may contain small quantities of carbon monoxid and hydrocarbons. To convert these compounds into carbon dioxid all of the gaseous products of combustion freed as completely as possible from water by passing through a condenser set obliquely on the neck of the combustion flask, are conducted through a combustion tube heated to low redness and filled with a mixture of copper oxid and lead chromate. The carbon compounds, now all converted into carbon dioxid, are absorbed in the usual way. To set up an apparatus of this kind the analyst should consult the figure in the second paper cited above.

345. **Estimation of Organic Hydrogen.**—The estimation of the total hydrogen is made without difficulty either by burning the

[41] Berichte der deutschen chemischen Gesellschaft, 1888, **21** : 2910, 1890, **28** : 2756.

sample in a current of oxygen or with pure lead chromate, and weighing the water produced. This water comes from two sources, the pre-existing water and organic hydrogen. There is no direct method of distinguishing one from the other. They may however, be estimated indirectly. The method of calculating the organic hydrogen has already been given (paragraph 333). Experience shows that the hydrogen thus calculated is a little greater than is necessary to form water with the whole of the oxygen found by 6.25, plus 6.2 per cent of the other organic carbon com-

The organic hydrogen is equivalent to 7.2 per cent of the nitrogeous constituents of the soil obtained by multiplying the nitrogen found by 16.25, plus 6.2 per cent of the other organic carbon compounds present calculated on the assumption that they contain 44.4 per cent of carbon. Thus, one gram of a soil that contains one per cent of protein and three per cent ligneous (carbohydrate) matter would contain

$$.01 \times .072 + .03 \times .062$$
$$= .00258 \text{ gram of hydrogen,}$$
or 2.58 milligrams.

346. Estimation of Organic Oxygen.—The determination of this oxygen cannot be made directly. It is obtained by calculation, according to Berthelot and André, from the oxygen in the proteid and ligneous matters, as follows:

Let p represent the weight of the proteid bodies in a sample of soil.

Then $O = \frac{p \times 33.5}{100}$.

Let $p' =$ weight of ligneous bodies.

Then $O' = \frac{p' \times 49.4}{100}$ and the total oxygen $= O + O'$.

An approximate result is thus obtained, very useful to have when account is taken of the oxidizing processes which go on in the soil during agricultural operations.

347. Estimation of Humus (Matière Noire.).—A common method of determining this substance is due to Grandeau.[42] The

[42] Traité d'Analyse des Matières agricoles, 3rd edition, 1897, 1 : 151.

soil is prepared for analysis by washing with dilute hydrochloric acid of a strength proportional to the quantity of carbonate. Where only a trace of carbonate exists acid of $^1/_{500}$ normal strength will suffice. After all the lime has been removed the acid is washed out with water and the washed soil is air-dried. The rest of the operation is carried on as follows: Ten grams of the fine earth, prepared as above, are mixed with coarse sand previously washed with acids and ignited. The mixture is placed in a small funnel, the bottom of which is filled with fragments of glass or porcelain. The mass is moistened with ammonia diluted with an equal volume of distilled water, and allowed to digest for three or four hours. The ammonia dissolves the humus without attacking the silica. The ammoniacal solution is displaced by treating the mass with pure water, or water to which some ammonia has been added, and the whole of the humus is thus obtained in a volume of from twenty to fifty cubic centimeters of filtrate. The filtrate is evaporated to dryness in a weighed platinum dish, and the weight of residue is determined and the percentage of humus calculated therefrom. The residue is incinerated, and when in sufficient quantity the phosphoric acid is determined in the ash. In soils poor in humus a larger quantity than ten grams may be used. If the soil be previously treated with hydrochloric acid, Grandeau recommends that the phosphoric acid be determined always in the ash of the dark matter.

The method has undergone various modifications and, as given by Hilgard, is now practiced as follows:[43]

About ten grams of soil are placed in a prepared filter. The soil should be covered with a piece of paper (a filter) so as to prevent it from packing when solvents are poured on it. It is now treated with hydrochloric acid from five-tenths per cent to one per cent strong (twenty-five and one-third cubic centimeters of strong acid and 808 cubic centimeters of water) to dissolve the lime and magnesia which prevent the humus from dissolving in the ammonia. Treat with the acid until there is no reaction for lime; then wash out the acid with water to neutral reaction. Dissolve the humus with weak ammonia water, prepared by diluting common satu-

[43] Bulletin 38, Division of Chemistry : 85.

rated ammonia water (178 cubic centimeters of ammonia to 422 cubic centimeters of water). Evaporate the humus solution to dryness in a weighed platinum dish at 100°; weigh, then ignite; the loss of weight gives the weight of humus.

The residue from ignition is carbonated with carbon dioxid, heated and weighed, thus giving the ash. It is then moistened with nitric acid and evaporated to dryness. The residue is treated with nitric acid and water, allowed to stand a few hours, and the solution filtered from the insoluble residue, which is ignited and weighed, giving the silica.

The soluble phosphoric acid is determined in the solution by the usual method, as magnesium pyrophosphate. It usually amounts to a fraction, varying from one-half to as little as one-tenth of the total in the soil. While the phosphoric acid so determined is manifestly more soluble and more available to vegetation than the rest of that found by extraction with stronger acid, it is clearly not as available as that which, when introduced in the form of superphosphates, exerts such striking effects even though forming a much smaller percentage of the whole soil. Nevertheless, very striking agreement in respect of the assimilation of phosphoric acid with actual practice is often found in making this determination.

The estimation of humus by combustion, in any form, of the total organic matter in the soil, gives results varying according to the season and having no direct relation to the active humus of the soil.

348. **Modification of Grandeau's Method for Determining Humus in Soils.**—According to Huston and McBride the function of the vegetable matter in the soil has long been a matter of contention among those interested in the science of agriculture. Two factors have contributed to the uncertainty existing in this matter: First, the very complex and varying nature of the compounds resulting from the decompostion of vegetable matter in the soils; and second, the lack of uniformity in the methods of determining either the total amount of organic matter present in a soil, or the amount that has been so far decomposed as to be of any immediate agricultural value. Prominent among these methods are those in

which a combustion is resorted to, the substance being either burned in air or in a combustion tube with some agent supplying oxygen. The loss on ignition is no measure of the amount of organic matter present since it is practically impossible to remove all the combined water from the soil previous to ignition, and neither of the methods gives information regarding the extent of the decomposition of the organic matter. Pure cellulose and the black matter of a fertile soil are of very different agricultural value.

Determinations of carbon in soils by oxidation with chromic and sulfuric acid, and with alkaline permanganate have been used. The method with alkaline permanganate agrees fairly well with combustion with copper oxid or lead chromate, but the chromic-sulfuric acid method gives only about 80 per cent of the carbon found by the combustion processes. Later investigations since the paper of Huston and McBride was written show that a much higher per cent of the carbon than that mentioned can be obtained by the chromic acid method. However valuable these processes may be for determining the total carbon in the soil, they furnish no information regarding the condition of the carbonaceous soil constituents, and as the determination is really one of carbon, the organic matter must be calculated by using an arbitrary factor. Generally the organic matter of the soil is considered to have 58 per cent carbon; yet different values are given ranging from 40 to 72 per cent.

There is a general opinion that the black or dark brown material of the soil, resulting from the decay of vegetable matter, has a much higher agricultural value than the undecomposed vegetable matter. No very sharp dividing line can be drawn, for changes in the soil are continually going on, and material may be found in almost every stage between pure cellulose and carbon dioxid. The character of the intermediate products will vary according to the conditions of tillage and the supply of air and water.

For agricultural purposes some means of determining the amount of decomposed matter is very desirable. Several solvents have been tried for this purpose. The earlier attempts were made by treating the soil with successive quantities of boiling half-saturated solution of sodium carbonate until the soil appeared to yield

no more coloring matter to the solvent. The solutions were then united, treated with hydrochloric acid, which precipitated the humic acid, which was then washed, dried, and weighed. This was considered the more soluble portion of the humic acid. The soil was afterward treated with caustic potash solution in the same manner, and the humus thus extracted was called insoluble humus. This last process was really more in the nature of manufacturing humus, for sawdust treated with caustic potash yields humic acid, and the inert organic matter in the soil was decomposed to some extent by the caustic alkali. Neither of the processes provided for the separation of the humic acid from the lime, magnesia, alumina, and iron with which it is usually combined in the soil.

In case results of different workers are to be compared, it is of the great importance that methods should be used that are of such a nature that errors resulting from difference of manipulation, and from difficulty of reproducing duplicate work can be reduced to a minimum.

Hence, a simple modification of the Grandeau method has been tried which has the advantage of keeping a definite amount of the soil in contact with a definite volume of ammonia for a fixed time, the strength of the ammonia remaining constant.

The process is as follows: The soil is washed with acid and water as usual. It is then washed into a 500 cubic centimeter cylinder, which is filled to the mark with ammonia of a given strength. The quantity of water used in washing the soil into the cylinder is to be considered in determining the strength of the ammoniacal solution, the cylinder closed and well shaken and allowed to remain for a definite time, usually 36 hours. The material is shaken at regular intervals. The cylinder is left inclined as much as possible without having the fluid touch the glass stopper, thus allowing the soil to settle on the side of the cylinder and exposing a very large surface to the action of the ammonia. During the last 12 hours the cylinder is placed in a vertical position to allow the soil to settle well before taking out the aliquot part of the solution. An aliquot portion of the clear ammoniacal solution is then witdrawn and submitted to analysis.

The process of washing the soil with hydrochloric acid and water is very tedious when performed in the usual way with the

wash-bottle. A simple automatic washing apparatus was devised by which a fixed volume of the washing fluid can be delivered at regular intervals, giving ample time for the thorough draining between each addition of the fluid, and requiring no attention. By this apparatus work can be continued day and night. Instead of washing on the usual form of filter paper in funnels, it is preferable with this apparatus to hold the soils on a disk of filter paper resting on a perforated porcelain disk in the bottom of the funnel. This removes the necessity of washing out the filter papers, does not permit of the accumulation of humus on the edge of the filter paper when the Grandeau process is used, and insures that all the washing fluids pass through the soil and not around it. This form of apparatus reduces the labor to a minimum and permits many determinations to be carried on at once.

This form of apparatus was only lately devised and has only been used long enough to test it and to show its advantages. The reported results were obtained by the ordinary methods of washing.

In all the work reported, five grams were used, as the soils contained so much humus that this amount gave enough humus for good work in the final weighings. The results obtained so far appear in the following tables:

TABLE I.—COMPARISON OF METHOD OF GRANDEAU WITH HUSTON'S MODIFICATION AND OF INFLUENCE OF STRENGTH OF AMMONIA SOLUTION. TIME OF DIGESTION IN MODIFIED METHOD THIRTY-SIX HOURS.

	Two per cent. NH_3.		Four per cent. NH_3.		Seven per cent. NH_3.		Eight per cent. NH_3.	
	Grandeau.	Huston.	Grandeau.	Huston.	Grandeau.	Huston.	Grandeau.	Huston.
1. Peat soil	....	....	16.40	20.06	....	....	....	....
Bogus soil.....	....	....	13.98	20.80	....	....	....	....
" "	....	....	17.43	....	....	....	....	....
Mean.....			15.94	20.43				
2. Peat subsoil.....	....	....	13.98	19.38	....	....	....	....
Bogus "	....	....	13.85	20.30	....	....	....	....
Mean.....			13.92	19.84				
3. Peat soil	9.05	15.60	14.71	21.24	19.77	21.70	16.05	21.42
Good "	10.27	15.88	15.34	20.20	19.85	21.90	15.40	21.80
Mean.....	9.61	15.74	15.03	20.72	19.81	21.80	15.73	21.61

4. Peat subsoil	....	....	16.75	24.34	....	....	....	....
Good "	....	....	18.60	23.52	....	....	....	....
Mean.			17.68	23.93				
5. Black soil, A	3.90	6.90	(1.86)	7.42	....	....	....	....
" " "	....	....	(1.67)	6.98	....	....	....	....
" " B	3.88	7.00	4.42	....	....	....	....	....
" " "	....	....	4.20	....	....	....	....	....
Mean... ..	3.99	6.95	(3.05)	7.20				
"			4.31					
6. Clay loam.....	1.86	4.20	2.40	4.26	2.14	4.02	1.85	4.12
West side, A.....	....	....	....	4.28	....	....	....	....
" " B.....	1.76	4.36	2.48	(3.40)	2.13	4.48	1.90	4.40
" " "	....	....	....	(3.10)	....	....	....	....
Mean.....	1.81	4.28	2.44	(3.76)	2.14	4.25	1.88	4.26
"				4.27				
7. Clay loam, A....	1.90	4.12	(1.60)	(4.59)	....	....	....	....
Lysimeter soil, B	1.61	4.22	(1.41)	(4.58)	....	....	....	....
" " C	....	....	1.80	4.12	....	....	....	....
" " D	....	....	1.95	4.04	....	....	....	...
" " E	....	....	1.92	3.85	....	....	....	....
" " F	....	....	1.95	4.08	....	....	....	....
" " G	....	....	1.90	3.93	....	...	....	....
" " H	....	....	1.90	3.80	....	....	....	....
Mean.....	1.76	4.17	(1.80)	(4.12)				
"			1.90	3.97				

NOTE.—Numbers in parentheses indicate results, generally the earliest ones, which the authors do not consider strictly comparable with the rest of the work. They are given solely for the purpose of exhibiting all the work that has been done to date. When a mean is included in parentheses it indicates that it is calculated from all the results obtained, including those not considered strictly comparable. "Bogus" is a name given to a peaty soil which is very sterile.

TABLE II.—INFLUENCE OF TIME OF DIGESTION. FOUR PER CENT OF AMMONIA USED THROUGHOUT. HUSTON'S METHOD.

	Thirty-six hours.	Forty-eight hours.	Sixty-eight hours.	Ninety-eight hours.
Peat soil.....	21.24	22.28	24.04	....
Good "	20.20	21.70	23.94	....
Mean	20.72	21.91	23.99	
Clay loam	4.28	4.00	....	4.40
" "	4.26	4.01	....	4.85
West side	(3.40)	....	....	....
" "	(3.05)	....	....	....
Mean.....	4.27	4.01		4.63

TABLE III.—RESULTS OF SUCCESSIVE EXTRACTIONS. TIME, ONE DAY FOR EACH EXTRACTION. GRANDEAU'S METHOD, FOUR PER CENT AMMONIA. PEAT SOIL.

		A. Per cent.	B. Per cent.	Mean. Per cent.	Remarks.
1st extraction,	750 cc....	16.90	18.96	17.93	
2nd "	250 "	2.80	2.38	2.59	
3rd "	250 "	1.77	1.10	1.44	
4th "	250 "	1.34	1.30	1.32	
5th "	250 "	0.89	0.85	0.87	
6th "	250 "	1.41	1.65	1.53	
7th "	250 "	2.10	1.80	1.95	Washed again with HCl for Ca. Trace found. HCl washed out, but trace of chlorids found in ash. Probably HCl absorbed from air as humus showed small quantity of a white volatile solid on evaporation.
8th "	250 "	0.67	0.65	0.66	
9th "	250 "	0.57	0.50	0.53	
Total.....	2750 "	28.45	29.19	28.82	

349. Summary of Results.—1. The modified method gives much higher results than the original method of Grandeau.

2. In the Grandeau method marked irregularities follow a change in the strength of the ammonia solution. These differences in results bear no relation to the strength of the solution used. They seem to be errors due to the difficulty of securing uniform and complete washing of the soil by the ammonia solution.

In the modified method the change in the strength of the ammonia solution makes practically no difference in the amount of humus extracted, except in the case of the peat where two per cent ammonia failed to extract all the humus. But the results show no considerable increase when the strength is increased to over four per cent.

3. The factor of time has not been fully investigated, but the results so far obtained indicate that the time exerts less influence in the modified than in the Grandeau method.

4. Table III shows that considerable quantities of the peat soil are still passing into solution in the Grandeau method at the end of ten days. With ordinary soils this is not true; but in the case of soil No. 5, a black soil, the solutions were colored at the end of a week. On the peat soil the modified method extracted from ten

to 50 per cent more than the Grandeau, and on the ordinary soil from two to three times as much humus.

5. In comparing duplicate results by both methods it is found that with soil No. 3 (peat), the following differences appear calculated to percentage of the total amount involved in the determination:

	Per cent.	Per cent.	Per cent.	Per cent.
Strength of ammonia.....	2.0	4.0	7.0	8.0
Modified method.....	1.7	5.0	1.0	1.8
Grandeau method.....	13.0	4.3	0.5	3.4

Spcial attention was paid to this point in case of No. 7, an ordinary soil; taking all results into consideration the greatest difference in percentage of total amount involved was, by the modified method, 19 per cent, and by the Grandeau, 30 per cent. In the set of six special determinations made by both methods to test this point and which are strictly comparable with each other, the maximum range was by the modified method 7.8 per cent and by the Grandeau 8.3 per cent of the total amount involved in the determination. From which it appears that the modified method is on the whole capable of yielding rather more concordant results than the Grandeau.

350. Official Method of Determining Humus.—The method of humus determination, adopted by the official chemists, is that of Huston and McBryde, with a few minor variations.[44]

Ten grams of the sample are extracted in a gooch with successive small quantities of a one per cent hydrochloric acid solution until the filtrate is shown to be free of lime on testing with ammonia and ammonium oxalate. The excess of acid is removed by washing with water.

The contents of the crucible, including the asbestos felt, are washed into a cylinder marked at 500 cubic centimeters with a four per cent solution of ammonia to the mark, and digested, after closing the mouth of the cylinder with its glass stopper and with frequent shaking for 24 hours. The cylinder is placed in an upright position for 12 hours, the supernatant liquor filtered, and an aliquot part taken for analysis. The sample is evaporated to dry-

[44] Bulletin 46, Bureau of Chemistry : 76.

ness and weighed after drying at 100°. After ignition the humus is calculated from loss of weight.

351. **Estimation of Free Humic Acids.**—This process, due to Müntz[45] is the forerunner of that of Huston and McBride. Twenty grams of the soil are reduced to a fine powder and saturated with 50 cubic centimeters of concentrated ammonia and allowed to digest two or three days in a warm place with frequent shaking. The volume is then made up to one liter with water, well shaken, and set aside for one day in order to permit the subsidence of the solid matter. At the end of this time 500 cubic centimeters of the supernatant liquor are acidified with hydrochloric acid in order to precipitate the humic bodies. The humus is collected on a filter, dried and weighed. It is then ignited and the weight of ash deducted from the first weight thus giving the actual weight of the humus obtained, free from mineral matter. This process gives the free humic acids. By previous treatment of the sample with hydrochloric acid as in the process of Huston and McBride, the total humus is obtained. The estimation of the free humic acids is of importance in determining the quantity of lime or marl which should be added to acid lands.

352. **Humus Method of van Bemmelén.**[46]—Van Bemmelén obtains the content of humus by the multiplication of the content of carbon in the soil by the factor of Wolff; *viz.*, 1.724. The estimation of carbon, water, and of the loss on ignition is conducted in combustion tubes in a current of oxygen. The nitrogen estimation is carried on according to the method of Dumas.

In soils containing calcium carbonate the organic carbon content is derived from the total carbon dioxid taken up by the potash bulbs during combustion (a); from other carbonates not decomposed on ignition and which are subsequently determined in the residue by treatment with hydrochloric acid in a carbon dioxid apparatus, (b), and the total carbon dioxid derived from the carbonates in the soil (c).

For each estimation from three to five grams of the soil are used, because with smaller quantities the errors of analysis too

[45] Encyclopédie chimique, **4** : 182.

[46] Die landwirtschaftlichen Versuchs-Stationen, 1890, **37** : 279 et seq.

strongly influence the results. The carbon is then calculated according to the formula:

$$\text{Carbon} = {}^{3}/_{11}\,(a + b - c).$$

The Carbon Dioxid of Carbonates.—It is necessary to expel the carbon dioxid at ordinary temperatures, because on heating to boiling, carbon dioxid would be formed from the humus. In a flask, as small as possible, the soil is treated at ordinary temperature, with dilute sulfuric or citric acid, the escaping gas dried over sulfuric acid, and taken up with soda-lime. Behind the soda-lime is a small tube filled with pieces of glass and moistened with sulfuric acid, which retains any moisture taken out of the soda-lime. A quantity of about one liter of air, free from carbon dioxid slowly drawn through the apparatus is sufficient to drive out all of the carbon dioxid when the estimation is made at ordinary temperatures.

A volcanic earth from Deli, which contained five per cent of humus, gave, at a temperature near 15°, 0.01 per cent CO_2. At boiling temperature two analyses gave 0.54 and 0.56 CO_2. This soil contained no carbonate, and the carbon dioxid found at the boiling temperature, must have come from the humus substances under the influence of the dilute acids.

A heavy clay containing 6.9 per cent of humus gave, at near 15°, 3.60 per cent CO_2; at 100° without boiling, it gave an additional 0.53 per cent, and with boiling an additional 0.11 per cent, or a total of 4.24 per cent CO_2. A light clay containing 3.2 per cent of humus, gave, at 15°, 5.09 per cent CO_2; at a boiling temperature an additional 0.43 per cent, and by continued boiling an additional 0.27 per cent.

353. Estimation of Humus by the German Method.—The German experiment stations follow the method of Loges,[47] depending on the oxidation of the humic bodies with copper oxid after evaporation of the sample with phosphoric acid. The object of the preliminary evaporation is to decompose the carbonates and set the humic acids free in order that they may be better and more easily oxidized than when burned in the combined state.

The sample of soil is placed in a Hoffmeister dish (schälchen),

[47] Die landwirtschaftlichen Versuchs-Stationen, 1883, **28** : 229, and 1891, **38**: 311.

moistened with dilute phosphoric acid and evaporated to complete dryness. The dish and its contents are rubbed up with pulverized copper oxid and placed in a combustion tube of 60 centimeters in length, open at both ends. There is then placed in the tube, and held in place by asbestos plugs, granular copper oxid to a length of 20 centimeters.

The combustion tube is placed in a proper furnace and one end connected with two washing-flasks, the first containing potash lye, and the other a solution of barium hydroxid. These flasks are to free the aspirated air from carbon dioxid. The other end of the combustion tube is connected with an appropriate apparatus for absorbing the carbon dioxid. Loges recommends the Pettenkofer absorption tube and a Fresenius drying cylinder.

Between the absorption apparatus and the aspirator, is also placed a washing-flask containing barium hydroxid solution, serving to detect any unabsorbed carbon dioxid. The layer of granular copper oxid is first heated, the air being slowly aspirated through the apparatus meanwhile, but not through the absorption bulbs. All the carbon dioxid is thus removed from the apparatus.

The absorption system being connected, the tube is heated slowly from the front, backwards, and after the tube is well heated a slow current of air is drawn through and continued until the combustion is complete, which is usually in about three-quarters of an hour.

After the tube is cool the powdered copper oxid and residue of combustion are removed, and for this reason the tube is stopped with a cork at both ends instead of being drawn out and sealed at one end. The tube can thus be refilled without disturbing the granular layer of copper oxid.

The drying cylinder used between the combustion tube and the absorption system has its upper part filled with cotton to avoid the deleterious effects of the nitric oxid produced in the combustion. With this arrangement the use of metallic copper in the combustion tube to reduce the nitric oxid can be dispensed with, the moist cotton holding back the acid fumes. The per cent of humus is obtained by multiplying the per cent of carbon found by 1.724.

354. Method of Raulin for the Estimation of Humus.[48]—The

[48] Comptes rendus, 1890, 110 : 289 et seq.

principle of this method rests upon the very feeble solubility in water of potassium phospho-molybdate and the greater solubility of the phospho-molybdates of sodium, magnesium, calcium, iron, and aluminum. The process does not require complex separations nor a very large quantity of soil. The volumetric estimation of humus in soil by a solution of potassium permanganate would be convenient and practical if the combustion of the organic matter were complete, and if the browning of the liquor did not render the end of the reaction uncertain. The process of Schmidt, modified as below, has given satisfactory results.

In a small flask, with flat bottom, containing about 250 cubic centimeters, are introduced ten cubic centimeters of a solution of manganese sulfate containing 16 grams of the anhydrous salt per liter, and ten cubic centimeters of a ten per cent solution of potassium permanganate. The solution is heated for a few minutes, the liquor is decolorized and manganese bronze (hydrated manganese dioxid) is precipitated. One hundred cubic centimeters of water and four cubic centimeters of sulfuric acid containing 150 cubic centimeters of monohydrated acid per liter are added. There is now added an exactly measured volume of the humic liquid properly prepared, so that in oxidizing completely it destroys at most only half of the manganese dioxid. The mixture is submitted to gentle ebullition for eight hours, the water being kept at a constant volume. The excess of manganese dioxid remaining is dissolved (hot) by a measured portion of decinormal oxalic acid in slight excess, and the excess of oxalic acid is oxidized by a solution of potassium permanganate containing one gram per liter. The volume of oxalic acid not consumed by manganese dioxid is calculated from the amount of permanganate consumed. The volume of oxalic acid, which corresponds to the same quantity of dioxid as the introduced humus, is also calculated by taking the difference between the volume of oxalic acid necessary to destroy all the dioxid formed by ten cubic centimeters of the ten per cent permanganate solution, and the volume of the oxalic acid which has destroyed the dioxid remaining after the action of the humus. The first volume of oxalic acid, that is to say, that which destroys the dioxid formed by ten cubic centimeters of ten per cent permanganate is determined in a preliminary titration.

moistened with dilute phosphoric acid and evaporated to complete dryness. The dish and its contents are rubbed up with pulverized copper oxid and placed in a combustion tube of 60 centimeters in length, open at both ends. There is then placed in the tube, and held in place by asbestos plugs, granular copper oxid to a length of 20 centimeters.

The combustion tube is placed in a proper furnace and one end connected with two washing-flasks, the first containing potash lye, and the other a solution of barium hydroxid. These flasks are to free the aspirated air from carbon dioxid. The other end of the combustion tube is connected with an appropriate apparatus for absorbing the carbon dioxid. Loges recommends the Pettenkofer absorption tube and a Fresenius drying cylinder.

Between the absorption apparatus and the aspirator, is also placed a washing-flask containing barium hydroxid solution, serving to detect any unabsorbed carbon dioxid. The layer of granular copper oxid is first heated, the air being slowly aspirated through the apparatus meanwhile, but not through the absorption bulbs. All the carbon dioxid is thus removed from the apparatus.

The absorption system being connected, the tube is heated slowly from the front, backwards, and after the tube is well heated a slow current of air is drawn through and continued until the combustion is complete, which is usually in about three-quarters of an hour.

After the tube is cool the powdered copper oxid and residue of combustion are removed, and for this reason the tube is stopped with a cork at both ends instead of being drawn out and sealed at one end. The tube can thus be refilled without disturbing the granular layer of copper oxid.

The drying cylinder used between the combustion tube and the absorption system has its upper part filled with cotton to avoid the deleterious effects of the nitric oxid produced in the combustion. With this arrangement the use of metallic copper in the combustion tube to reduce the nitric oxid can be dispensed with, the moist cotton holding back the acid fumes. The per cent of humus is obtained by multiplying the per cent of carbon found by 1.724.

354. Method of Raulin for the Estimation of Humus.[48]—The

[48] Comptes rendus, 1890, **110** : 289 et seq.

principle of this method rests upon the very feeble solubility in water of potassium phospho-molybdate and the greater solubility of the phospho-molybdates of sodium, magnesium, calcium, iron, and aluminum. The process does not require complex separations nor a very large quantity of soil. The volumetric estimation of humus in soil by a solution of potassium permanganate would be convenient and practical if the combustion of the organic matter were complete, and if the browning of the liquor did not render the end of the reaction uncertain. The process of Schmidt, modified as below, has given satisfactory results.

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In regard to the humic liquor, it is prepared by treating ten grams of earth with soda solution in the usual manner. It will be easy to calculate the volume of the oxalic solution equivalent to the total volume of the humic solution, of which a determined fraction has been assayed, and consequently the volume of oxalic solution equivalent to the humus in ten grams of the dry earth. This number of cubic centimeters of the decinormal oxalic solution multiplied by 0.8 will express in milligrams the weight of oxygen necessary to burn the humus from ten grams of dry earth. Humus not being a definite compound, but a residue of complex organic matters partially oxidized, it will require as much more oxygen to complete the combustion as the previous oxidation has been less pronounced. This weight of oxygen necessary to burn the humus from ten grams of dry earth may serve to show the total value as well as the weight of the humus itself. However, if we wish to have directly the weight of the humus, resource can be had to a table which, without being rigorous, can be regarded as sufficiently exact when the variability of the constitution of humus is taken into account.

Volume of decinormal oxalic acid for 10 grams of dry earth. cc.	Corresponding humus, directly determined. mg.	Volume of decinormal oxalic acid for 10 grams of earth. cc.	Corresponding humus directly determined. mg.
50	80	1600	1560
100	150	1800	1720
200	280	2000	1890
300	400	2500	2315
400	510	3000	2735
500	610	3500	3170
600	705	4000	3605
700	790	4500	4035
800	885	5000	4460
900	975	5500	4890
1000	1060	6000	5310
1200	1225	6500	5745
1400	1390		

355. **Pasturel's Method.**—According to Pasturel[49] the process of Raulin does not furnish figures that are rigorously exact except with soil of which the humus contains 45 per cent of carbon. When the richness in organic carbon is less, the results of the esti-

[49] Annales agronomiques, 1890, **16** : 558 et seq.

mation are too high. Pasturel modifies the process as follows:

Manganese Sulfate.—Dissolve 16 grams of the pure anhydrous manganese sulfate in distilled water and make the solution up to one liter.

Potassium Permanganate.—Make a solution of ten grams of potassium permanganate in one liter of water; 100 cubic centimeters of the liquor just mentioned are diluted to one liter and constitute the potassium permanganate solution one to ten.

Oxalic and Sulfuric Acids.—A solution of oxalic acid is prepared containing 6.3 grams of the acid in one liter of water, and a dilute solution of sulfuric acid, by dissolving 150 grams of the monohydrated acid in one liter of water.

Humus Solution.—The solution of humus is prepared by the following process: Ten grams of fine earth are freed from all their carbonates by dilute hydrochloric acid. After washing, the filter is broken and the dirt is washed into a small flask. Not more than 20 or 30 cubic centimeters of water should be employed for this purpose. Twenty cubic centimeters of a liquor containing two grams of caustic soda are added, and the flask is placed upon a sand-bath and maintained at a boiling temperature for six hours. It is then diluted with water, filtered and washed as long as the waters are colored. The liquor is treated with dilute sulfuric acid until almost the whole of the soda is saturated. It is indispensable, however, to maintain a slight alkalinity in order that the organic matter may rest totally dissolved. The precipitation of flocculent silica which is almost always produced is without inconvenience. Afterward the volume is completed to 500 cubic centimeters and the humus solution is then ready for use.

Estimation of the Humus.—Ten cubic centimeters of the manganese sulfate are placed in a flask and ten cubic centimeters of the permanganate added, and the whole is then slightly heated, and afterward 100 cubic centimeters of water and four cubic centimeters of sulfuric acid are added. The humic liquor is now introduced in such proportion that the humus which it contains dissolves at the greatest, a half of the precipitated manganese and the rest of the process is continued as described by Raulin.

The principle objection to these two processes is evidently the

manner in which the humus solutions are prepared. The tendency to produce humus bodies on heating organic matter (carbohydrate) with a fixed alkali has already been pointed out. The methods of Raulin and Pasturel, therefore, are not such as promise the most accurate results.

356. The Estimation of Soil Acidity to Determine Quantity of Lime.—Within the past few years, it has been definitely shown that the reaction of a soil exerts a marked influence on its crop-producing power. While the reaction affects the chemical and the physical condition of the soil to a considerable extent, the growth of plants is more directly affected by the action of the acids on the plant roots, and upon the micro-organisms of the soil.

The importance of the matter has led to the elaboration of several methods for determining the amount of acids in soil, but, owing to the exceedingly small amount usually present in ordinary arable soils, the influence of other material, and the constant changes taking place in the soil, none of these methods has shown a close relation between crop production and the amount of acidity as determined by any of the methods.

The usual method of determining whether a soil is acid or not is to press a piece of delicate blue litmus paper against the moistened soil and note the rapidity with which the color is changed to pink. A somewhat more delicate method, particularly with soils which contain practically no free acids but are yet in need of liming, is the following proposed by Veitch:[50]

About ten grams of soil are treated with 100 cubic centimeters of distilled water in a Jena flask and allowed to stand over night. Fifty cubic centimeters of the supernatant liquid are carefully drawn off and boiled with a few drops of phenolphthaleïn in a covered Jena beaker until the appearance of the pink color or to a volume of about five cubic centimeters with no development of color. The pink color shows the soil to be alkaline, while no color shows it to be acid or neutral.

Wheeler, Hartwell and Sargent[51] have recently made a critical examination of the methods which have been proposed for this purpose, checking the chemical methods by field experiments.

[50] Journal American Chemical Society, 1904, **26** : 661.

[51] Journal American Chemical Society, 1900, **22** : 153.

These investigators were unable to correlate the chemical results obtained by any of the methods examined with the field results, but regarded as promising the titration of dilute ammonia which had been in contact with the soil for some time, and also a modification of the method of Tacke based on the evolution and estimation of the carbon dioxid freed from calcium carbonate by the acid soil on boiling them together in water.

357. Method of Tacke.[52]—This method designed primarily for determining the free acids in moor soils consists essentially in expelling the carbon dioxid from calcium carbonate brought in contact with the soil at ordinary room temperature.

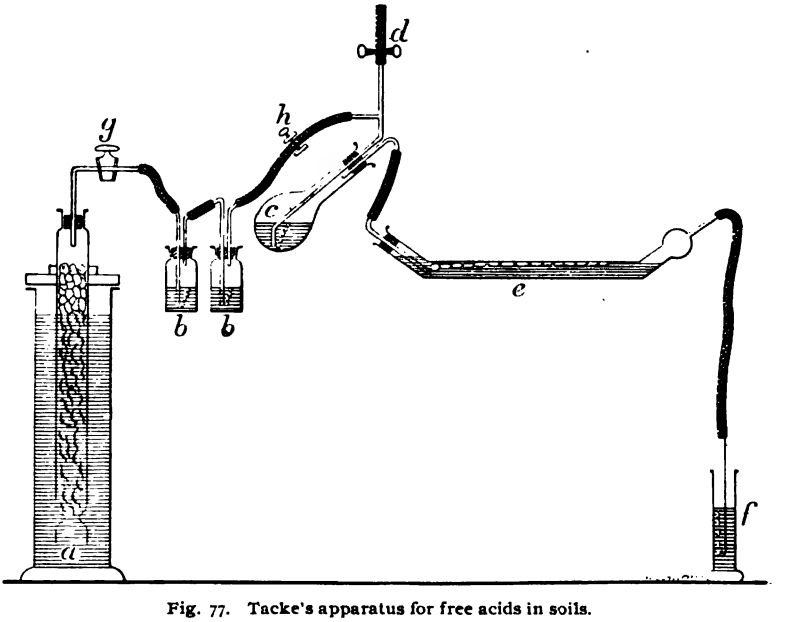

Fig. 77. Tacke's apparatus for free acids in soils.

The apparatus employed by Tacke is illustrated in figure 77. The decomposition flask *c* contains the finely divided fresh peat soil whose acidity is to be determined. The air is removed from *c* by a stream of hydrogen generated in *a*, and washed in *b b*, containing, respectively, acid and alkaline solutions. The hydrogen escaping from *c* passes through a Pettenkofer absorption tube *e*

[52] Chemiker Zeitung, 1897, **21** : 174.

and enters into the vessel *f* under water. The stream of gas is regulated by the pinch-cock *h* and by lowering or raising the exit tube in *f*. The three way tube entering *c* also carries a pinch-cock *d*, by means of which the carbonate of lime, in the form of suspended silt, can be introduced into *c*. The sample of peat soil, and from 100 to 200 cubic centimeters of water are placed in *c* and the whole system subjected to the action of the hydrogen for about an hour in order to remove any oxygen or carbon dioxid which may be present. For wetting the suspended silt freshly boiled water is employed, and also the liquid for generating the hydrogen must be freshly boiled before using. *e* contains about 100 cubic centimeters of $N/_5$ or $N/_{10}$ soda lye. An excess of suspended carbonate of lime is added through *d*, care being taken to admit no air, and the contents of *c* are thoroughly mixed by shaking, and the stream of hydrogen continued for three additional hours. The contents of *e* are brought into a beaker and titrated with $N/_5$ or $N/_{10}$ hydrochloric acid, using phenolphthalein as indicator.

Or the liquid is finally removed from the tube, avoiding the absorption of carbon dioxid from the air, barium chlorid added and the solution titrated with $N/_5$ or $N/_{10}$ hydrochloric acid using phenolphthalein as an indicator with attention to the points brought out by the investigations by Küster[53] and by Lunge[54].

The acidity of several samples of peaty soils was determined by this method, and found to vary from 1.72 per cent to 2.24 per cent. The practical application of this method would lead at once to the determination of the proper amount of lime which should be added for the neutralization of the acidity in the peaty soil.

For example, a soil which in the circumstances described above, yields 1.70 per cent of carbon dioxid indicates a need of about 4,000 kilos of lime per hectare. The acidity of the peat thus determined has also important bearings on the behavior of the soil with slag and natural phosphates.

Wheeler's modification of this method consists of boiling in water the mixed soil and calcium carbonate and determining the carbon dioxid evolved, but elimination of carbon dioxid continues

[53] Zeitschrift für anorganische Chemie, 1896-7, **18** : 127.

[54] Zeitschrift für angewandte Chemie, 1897, **10** : 3.

indefinitely owing to reactions between the soil constituents and the calcium carbonate. Vietch has found that even an alkaline soil containing calcium carbonate will continue to evolve carbon dioxid when treated in the same manner.

HOPKIN'S METHOD.

This method was proposed at the 19th meeting of the Association of Official Agricultural Chemists[55] by Hopkins and his associates of the Illinois station. It is based upon the reaction which occurs when solutions of mineral salts are added to an acid soil. The organic acids of the soil are themselves very difficultly soluble, and it is practically impossible to completely extract them from the soil with distilled water, even though large quantities of water be percolated through the soil; but, when a mineral salt solution is added to the soil, the organic acids (humic acid, etc.,) unite with the mineral base, forming neutral humates, etc., and liberating the mineral acid, which, of course, is perfectly soluble, and whose titrating power furnishes a basis for determining the total acidity of the soil. The method consists in shaking 100 grams of soil with 250 cubic centimeters of five per cent sodium chlorid solution for three hours and titrating 125 cubic centimeters of the boiled, clear filtrate with standard alkali, using phenolphthalein as indicator. The result multiplied by four equals the acidity in terms of cubic centimeters of standard alkali required to neutralize 100 grams of soil. The factor four is used in place of the natural factor two, because by repeatedly removing one-half of the clear salt solution, restoring the volume with five per cent salt solution, shaking and titrating as before, it is found that the total alkali required for 100 grams of soil averages approximately four times the first titration.

Veitch[56] has recently studied the method very thoroughly and finds that there is no setting free of appreciable quantities of hydrochloric acid and that there is practically no reaction between the organic matter and the salt solution, whereby difficultly soluble organic acids are dissolved, but that the acidity of the filtrate (or that acidity which is greater than would be given by water under the same conditions) is due chiefly to the solution of alumina or some other base yielding an acid-salt. It appears that the hydrated

[55] Bulletin No. 73, Bureau of Chemistry.

[56] Journal of the Ameriean Chemical Society, 1904, 26 : 637.

neutral silicates or aluminates are quite strongly attacked by the salt solution, resulting in the replacement of aluminum by sodium, or a breaking-up of the compound, and the consequent formation of an acid solution of aluminum chlorid, the titration of which, with alkali, constitutes the apparent acidity as determined by this method.

It was found that the ratio between successive filtrates is not a constant one, but varies considerably. Hopkins, *et al.*, found it to vary from 0.62 to 0.8, and Veitch found it to vary from about .6 to 1.

The method is very simple in execution, and for this reason very attractive to the busy chemist. It is not, however, a method which determines the total apparent acidity of a soil, nor can it be said that it determines the acidity injurious to sensitive crops.

By this method an approximate determination of the amount of aluminum or other acid-salt forming bases dissolved by sodium chlorid under the conditions of the method can be secured, and the lime required to neutralize such acid-salts be calculated. But as different salts and different concentrations of the same salts dissolve different quantities of these bases, it can not be assumed from chemical data that lime would act in the same way that normal sodium chlorid does, nor that the action of sodium chlorid is a final measure of the lime requirements of soil.

358. **The Lime-Water Method.**—This method is a modification of the method of Tacke[57] and is based on the fact that after the affinity of the soil for calcium as bicarbonate is satisfied, the presence of the slightest amount of this salt is manifest by the pink color produced when phenolphthaleïn is boiled with a portion of the water which has been in contact with the treated soil.[58] It is claimed for this method that it represents the maximum lime requirements of a soil.

The method of manipulation is as follows:—

To three portions of soil, each consisting of as many grams as the standard lime-water contains tenths milligram of lime (CaO) per cubic centimeter, add from 50 to 60 cubic centimeters of dis-

[57] Chemiker Zeitung. 1897, **21** : 174.

[58] Vietch, Journal of the American Chemical Society, 1904, **26** : 637 et seq.

tilled water and different amounts of standard lime-water. For example, to the first add ten cubic centimeters, to the second 20 cubic centimeters, and to the third 30 cubic centimeters of lime-water. Evaporate on the steam-bath, transfer to stoppered Jena flasks with 100 cubic centimeters of distilled water, allow to stand 15 hours, with occasional shaking, draw off 50 cubic centimeters, place in a Jena beaker, add a few drops of phenolphthaleïn solution, and boil until the appearance of the pink color, or in case no color is developed, to a volume of about five cubic centimeters. Then with two portions of treated soils, one of which has been rendered alkaline by the lime-water and the other of which is still acid, as guides, prepare three fresh portions of ten grams each and add lime-water as before, except that the amount added to one dish differs from that added to another by one or two cubic centimeters. Dry, take up with 100 cubic centimeters of water, allow to stand, draw off, and treat exactly as before. The smallest amount of lime-water which gives the characteristic pink color is taken as the acidity equivalent of the soil. Each cubic centimeter of standard lime-water is equivalent to an acidity of 0.01 per cent expressed as calcium oxid.

The most serious objection to the method, from the analyst's standpoint, is the number of determinations which must frequently be made before the end point is reached.

In the practice of the lime-water method it has been found that the length of time the treated and dried soil is allowed to stand in contact with water has a considerable effect on the apparent acidity as determined by this method. When the treatment continues from 48 to 72 hours, the pink color with phenolphthaleïn is developed with less added lime-water than where the solution is allowed to stand 16 hours or less, so that some soils which are acid when allowed to stand 16 hours give an alkaline filtrate when allowed to stand from 24 to 48 hours longer.

These results appear to be due to the slow solubility and hydrolyzation of the neutral lime compounds that are formed with the added lime-water, or to the solution and hydrolyzation of neutral compounds already present in the soil. It has long been believed that the bases of the soil go into solution partly as bicarbon-

"acidity" in soils is very general. Most soils, even those common minerals, particularly the zeolites and feldspars, when reduced to fine powder and treated with carbon dioxid free water, gave a more or less strong reaction with phenolphthalein.

Both of these classes of minerals are believed to be present in most soils, but from the nature of the origin of soils the more soluble forms are not likely to be present in considerable amounts, nor are the more insoluble forms likely to be present in a finely divided state. Hence the solution of such minerals would be expected to be slow and the development of an alkaline reaction on long standing, with smaller amounts of lime-water, might be thus accounted for.

359. **Nature of Soil Acidity.**—Our knowledge the nature of "acidity" in soils is very general. Most soils, even those which would be reckoned as very acid by any of the various methods which have been proposed for determining soil acidity, contain but little water-soluble acids or acid salts. Practical farm experience has strongly indicated that the acids which may be removed from soils by simple treatment with water are not the total harmful acids which they may contain. It has been assumed that very difficultly soluble organic acids as "humic," "ulmic," etc., and their acid salts, the "humates," "ulmates," etc., are chiefly responsible for the harmful acidity of soils, and it has been the object in devising methods for determining soil acidity to reach such compounds.

Veitch[60] in a careful comparison of the sodium chlorid method and the lime-water method has shown that such compounds are not the only ones which go to make up soil acidity, that there is no close relation between the "acidity" as determined by either of the methods and the toxicity of such acidity, and concludes that acidity, as determined by these methods, cannot be of the same nature in all soils.

Until we have more definite evidence as to the nature and effect of the various compounds which are reckoned as constituting a part of the total apparent acidity of soils, he suggests tentative-

[59] American Journal of Science and Arts, 1845, **5** : 5.

[60] Journal of the American Chemical Society, 1904, **26** : 661.

ly and for purposes of further study the following classification of acidity.

Active or actual acidity, due to relatively soluble organic and inorganic acids and acid salts; and *inactive or negative acidity,* reaching, in some soils actual neutrality, as determined by the usual indicators. This later condition, constituting a part of the absorptive power of soils, appears to be due to the presence of certain constituents, such as the easily attacked hydrated or colloidal silicates, and many non-acid organic compounds, which have a strong affinity for sodium, potassium, calcium, and magnesium. On solution of these bases by the soil water, or on their addition in alkaline compounds they combine immediately with these practically neutral constituents, which thus prevent the reaction of the soil from becoming alkaline until the above-mentioned affinity is satisfied. This condition, while harmful to sensitive plants, is certainly not so harmful as the condition due to free acids or acid salts. Further than this, the reaction which takes place between certain of these soil constituents and added chlorids, sulfates, etc., produces positively acid salts, as we have seen from the reactions of the sodium chlorid method. There can be but little doubt that it is due partly, at least, to the acidity thus produced that the injury arising from the use of chlorids and ammonium sulfate on acid or neutral soils, is to be ascribed.

If it is true that crops are most profitably produced only when the soil is completely neutralized or faintly alkaline, the separation and estimation of the several components of the total apparent acidity is not of much practical importance. On the other hand, if it is not necessary to completely neutralize the total apparent acidity, it becomes necessary to devise methods for the estimation of the harmful acidity, and determine to what it is due.

As a beginning along this line the water-soluble acids and acid salts may be determined. The negative acidity due to easily attacked silicates may be estimated by means of the sodium chlorid method, using a proper correcting factor. The total apparent acidity may be determined by the lime-water method, and by subtracting the acidity determined by the sodium chlorid method, the acidity due to insoluble organic matter is ascertained.

360. Estimation of Carbonates in Arable Soil.—The principle of the determination depends on the liberation of the carbon dioxid from its compounds in the soil by acting on them with an acid, which is capable of displacing the carbonic acid and the desiccation, absorption, and weighing or measuring the evolved gas. Any of the ordianry forms of apparatus for estimating carbon dioxid may be used in this determination.

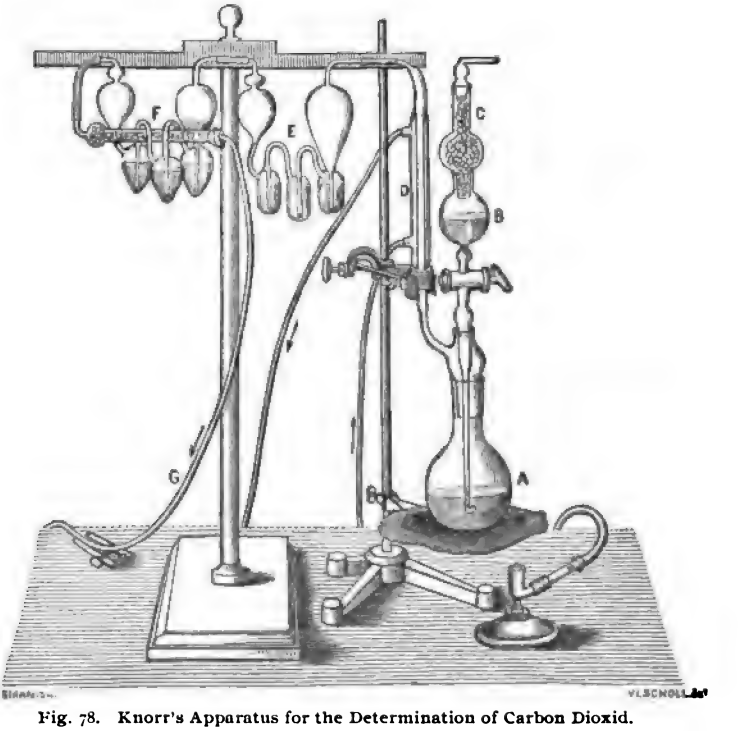

Fig. 78. Knorr's Apparatus for the Determination of Carbon Dioxid.

The apparatus of Knorr[61] has been used with satisfaction for many years in the laboratory of the Department of Agriculture.

The apparatus consists of a flask A, Fig. 78, in which the carbon dioxid in the soil is liberated. A condenser, D, fits by means of a ground-glass joint into the neck of the flask in which the liberated gas, together with any air or aqueous vapor which may be

[61] Bulletin No. 13, Division of Chemistry : 590.

carried forward, is cooled. This prevents any excess of vapor of water from entering the absorbing bulbs, which could easily happen at the end of the experiment when the contents of A are raised to the boiling point. The bulb B contains the acid, usually hydrochloric, which is employed for decomposing the carbonates. It is provided with a guard bulb-tube, C, the contents of which serve to absorb any carbon dioxid which might enter the apparatus with the air during aspiration at the close of the determination. The carbon dioxid is dried in the bulb-tube, E, in oil of vitriol, and absorbed in the potash solution in F. It is advisable to aspirate a slow current of air through the apparatus by means of the tube G during the whole of the operation. The quantity of the sample to be taken depends on its richness in carbonates. Many soils are so poor in carbonates as to render any attempt at exact determination nugatory. On the other hand, a comparatively small sample of marls will be sufficient. A preliminary qualitative test will indicate, in a genral way, the quantity of the sample to be used. The sample of soil, from five to 50 grams, according to its content of carbonates, having been transferred to A, which should be perfectly dry, is made into a batter with freshly boiled distilled water. When all the parts of the apparatus are properly connected gas-tight, the cock between B and A is slowly opened and the hydrochloric (nitric) acid in B allowed to flow into A at such a rate as will secure a moderate evolution of gas.

When the carbonate is entirely decomposed, a lamp is brought under A and its contents gradually raised to the boiling point. The aspiration of air, free from carbon dioxid, is meanwhile continued until all the liberated gas has been absorbed in F. Usually about 15 minutes will be sufficient to accomplish this purpose.

361. Bernard's Calcimeter.—For a rapid and approximately accurate method of determining the amount of carbonate in the soil, estimated as calcium carbonate, Bernard makes use of the well-known method of the volumetric estimation of carbon dioxid. The sample to be examined should not be powdered in any way. The sample in a natural state, well air-dried, is gently broken up by the fingers and passed through a sieve having ten meshes to the centimeter. Of the fine earth thus obtained, one gram is taken for

the determination. If the percentage of carbonate in the soil exceeds 50 then only half a gram is taken.

The apparatus employed is one well known. The small erlenmeyer C is fitted with a rubber stopper carrying an exit tube for the gas and a small thermometer. This flask is connected by means of a rubber tube and small glass tube to the measuring burette B. This burette is graduated from 0 to 100 cubic centimeters. Below, by means of a rubber tube, it is connected with the open bulb, A, which, by means of a cord about its neck, can be suspended by the hook as shown in the figure. The measuring tube is filled with water through A until the level of the liquid in B is slightly above the zero mark. Meanwhile the one gram of earth has been placed in C, together with the tube D three-fourths filled with an equal mixture of water and strong hydrochloric

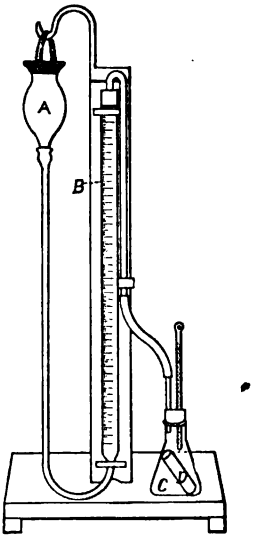

Fig. 79. Bernard's Calcimeter.

acid. The greatest care must be taken that no part of the acid be spilled.

The rubber stopper is now forced into C until the level of the water in B is just at the zero mark. Grasping C in the right hand and A in the left, the operator inclines C until the contents of D

are emptied. Meanwhile as the gas is evolved, A is lowered at such a rate as to always keep the level of the water in B and A on the same plane. In a few moments the evolution of gas is complete, and the volume given off is read at once without correction. This volume multiplied by 0.4 gives the percentage of carbonate in the sample examined. It is understood that the determination is made at ordinary temperatures; *viz.*, 17° to 22°. Example:

The above method is useful in the classification of chalky soils and in determining approximately the quantity of calcium carbonate which they contain. It is of little value in the study of soils containing but little carbonate or compounds of carbonic acid decomposed with difficulty in the cold. Moreover, in the cold a notable quantity of the gas remains dissolved in the dilute acid and is absorbed by the water used in the preliminary moistening of the soil.

362. Soils Deficient in Carbonates.—When a soil contains but a small quantity of carbonates, Müller[62] has called attention to the fact that the carbon dioxid absorbed by the water in which the soil is rubbed up may vitiate the result. Instead of water a titrated solution of sodium carbonate is employed. The apparatus is composed of a flask containing the mixture of the sodium carbonate and the soil on which the hydrochloric acid is to act. The hydrochloric acid is contained in a small tube, as in the apparatus described above. The gas is received in a rubber tube 1.5 meters long and from three to four millimeters interior diameter, and connected with a burette, the open mouth of which dips into the water of a cylinder of proper length. The volume of gas is read when the burette is raised or lowered in the cylinder until the liquid within and without stands at the same level.

During the action of the acid on the carbonates the flask is constantly shaken.

Several readings of the volume of gas are made, the evolution flask being vigorously shaken before each one. Finally, in order to allow for the variations in temperature and pressure of the ex-

One gram of a sample treated as above, gave of carbon dioxid (uncorrected) 65 cc. $65 \times 0.4 = 26.00$ per cent. calcium carbonate in sample.

[62] Bulletin de la Société chimique de Paris, 1889, [3], **2** : 483.

terior air which may take place between the beginning and the end of the reaction, a second flask containing air is placed by the side of the evolution flask and communicating with a narrow U-tube half filled with water. Any variations in the volume of the air in the flask will be shown by variations in the height of the liquid in the two arms of the U-tube, and the volume of the variation can be easily determined by having the U-tube calibrated.

If now a equals the volume per cent of carbon dioxid in the atmosphere of the evolution flask at the end of the reaction, v the volume of gas disengaged, and V the volume of the atmosphere in the evolution flask, the per cent of carbon dioxid contained in a given length of the rubber tube will be equal to $\frac{a}{2}$. This arises from the fact that the first gas which passes into the rubber tube is composed solely of air, while the last contains a per cent of carbon dioxid. By reason of the shaking of the flask the mean richness of the contents of the tube in carbon dioxid, will be sensibly $\frac{a}{2}$.

From the above data the following equations are derived:

1. $v\frac{a}{2} + Va = v.$

2. $a = \frac{v}{\frac{v}{2} + V}.$

If the weight of the carbon dioxid dissolved in V′ cubic centimeters of the liquid in the evolution flask be represented by q, the coefficient of the solubility of pure carbon dioxid in this liquid will be, according to the law of the solubility of a gas, equal to $k = \frac{q}{V'a}$.

The value of k has been determined for various strengths of the sodium carbonate solution, using five cubic centimeters of hydrochloric acid containing 1.6 grams pure hydrochloric acid. For solutions disengaging from five to fifty milligrams of carbon dioxid, the mean value of k is found to be 1.8 milligrams in the absence of calcium chlorid. When calcium chlorid is present in quantities varying from 0.03 to 0.07 gram per cubic centimeter of liquid in the evolution flask, the value of k is 1.4 milligrams.

By adopting, according to circumstances, the one or the other of the above numbers and multiplying it by Va, as determined by experiment, results are obtained differing only 0.2 to 0.3 milligram from those secured by direct weighing of the evolved gas.

Dietrich[63] at a much earlier date called attention to the necessity of adding the volume of the dissolved gas to the measured volume in such determinations, and this volume or weight is easily determined by the above formulas.

364. **Belgian Method.**—The method pursued at the Gembloux Station[64] consists in rubbing up from five to 50 grams of the sample of soil, according to its contents in carbonate, in a porcelain dish with distilled water in order to make a thin paste. The mass is worked to drive out all the air, the whole washed into a flask of 300 cubic centimeters capacity, and the amount of carbon dioxid estimated by setting free with an acid, and collecting the carbon dioxid evolved in potash bulbs.

DIGESTION OF SOILS WITH SOLVENTS.

365. **General Considerations.**—There are two points in connection with the determination of mineral matters in the soil which must always be kept in view; *viz.*, first, the estimation of the total quantities of material in the soil, and second, the study of those materials which are more easily brought into solution and thus made available for the food of plants.

It is well understood that the soil particles do not give up entirely to the plant the food materials which they contain. The practical value therefore of an analysis of a soil depends more upon the exact determination of the plant food available than upon its total quantity. From a mineral and geological point of view, on the other hand, an idea of the total composition of the soil is the object to be attained.

For the determination of the available plant food, various solvents have been proposed, none of which, perhaps, imitates very accurately the natural solvent action of organic life and moisture on the soil materials. A description of the standard methods of

[63] Zeitschrift für analytische Chemie, 1864, 8 : 162 et seq.

[64] Petermann, L'Analyse du Sol : 20.

preparing soil extracts will be the subject of a few succeeding paragraphs. The solvents which have been prepared and used include water, water containing carbon dioxid, solutions of organic acids, solutions of salts of ammonia, mineral acids, hydrofluoric acid and carbonates of the alkalies and other solvents.

366. Estimation of the Quality of Materials Soluble in Water and Other Weak Reagents.[65]—Five hundred grams of the air-dried soil are treated in a flask with 1,500 cubic centimeters of water, less the quantity of water already contained in the air-dried soil which is volatile at 125°. The mass is frequently shaken, and, after 72 hours, 750 cubic centimeters of the liquid filtered. The filtrate is evaporated to dryness in a platinum dish, dried at 120° and weighed. This is then incinerated and, after treatment with ammonium carbonate and gentle ignition, is again weighed. The further examination of the residue for acids and bases is made by some of the methods hereafter described.

Treatment with Water Saturated with Carbon Dioxid.—Two thousand five hundred grams of the air-dried soil are treated with 8,000 cubic centimeters of distilled, and afterwards with 2,000 cubic centimeters of water, which have previously, at room temperature, been saturated with carbon dioxid. The mixture is left in a closed flask for seven days, frequently shaken, after which 7,500 cubic centimeters of the liquid are filtered. The clear filtrate, after treatment with a little hydrochloric acid and a few drops of nitric acid, is evaporated to dryness. After the separation of the silica the traces of iron, alumina, lime, sulfuric acid, magnesia, potash, and soda, are estimated in the liquid in the manner hereinafter to be described. Phosphoric acid is always present in such a case but in such small quantities as to make its estimation a matter of some difficulty.

Treatment with Water Containing Ammonium Chlorid.—In the flask containing the residue from the last experiment; *viz.*, the soil with 2,500 cubic centimeters of liquid, are added 1,500 cubic centimeters of water saturated with carbon dioxid, and 8,000 cubic centimeters of pure water in which five grams of ammonium chlorid are dissolved. The mixture is then left for seven

[65] Zeitschrift für analytische Chemie, 1864, 3 : 97.

days, with frequent shaking, and 7,500 cubic centimeters of the liquid are then filtered, and the substances dissolved, determined in the filtrate. In addition to the usual quantities of lime and magnesia, from two to four times as much alkali is dissolved by this treatment as is found in the solution from the water containing carbon dioxid alone.

Treatment with Water Containing Acetic Acid.—The acetic acid should be of such a strength that after it has fully acted on the soil it should still contain 20 per cent of free acid. One thousand grams of the soil dried at 100° are used and the acid added in proper proportions and treated in the manner to be described for determining the solvent action of hydrochloric acid.

367. Treatment with Citric Acid Solution.—In ascertaining the quantities of soil materials soluble in a solution of citric acid, Dyer[66] recommends the use of a solution of one per cent strength. The digestion is carried on as follows: Place in a flask or bottle, holding about three liters, 200 grams of air-dried soil and two liters of distilled water, in which are dissolved 20 grams of pure citric acid. The soil is left, at room temperature, in contact with the one per cent acid for seven days, with thorough shaking several times a day. Each sample is shaken approximately 400 times. At the end of the digestion the solution is filtered and 500 cubic centimeters of the filtrate, corresponding to 50 grams of the soil, are used for analysis for each ingredient to be determined.

The digestion in citric acid is especially recommended by Dyer because of its supposed near resemblance to the methods of solution of plant food in contact with the rootlets of plants. It is evident, however, that this process is in no sense an imitation of natural methods. The solution is used chiefly for the estimation of potash and phosphoric acid. Dyer concludes, from a comparison of the action of a solution of citric acid on soils of known fertility, that when as little as 0.01 per cent of phosphoric acid is dissolved from a soil by this treatment it is justifiable to assume that it stands in immediate need of phosphatic manure. The methods used by Dyer to determine the phosphoric acid and potash in the citric acid solution will be given in their appropriate place.

[66] Journal of the Chemical Society, Transactions, 1894, **65** : 115.

368. Comparison of Some Common Methods of Extracting Soils with Weak Solvents.—In view of the fact that many methods of extracting from the soil mineral elements which are important to the growth of plants have been proposed, Hall and Plymen have subjected the more common of them to comparative tests.[67]

Of the common methods compared; *viz.*, (a) extraction with a one per cent citric acid solution, (b) with corresponding quantities of hydrochloric and acetic acids, (c) with a saturated solution of carbonic acid, and (d) within an ammoniacal solution of ammonia citrate they recommend as the process giving results most in harmony with field results the method (a).

Ingle has subjected soils extracted with citric acid to pot cultures and shown that such soils have lost the greater part of their fertility.[68]

Attention is called to the fact, however, that changing conditions of temperature, rainfall and sunshine must be taken into consideration in the interpretation of the data obtained.

369. Treatment with Hydrochloric Acid.—The solutions of soils usually subjected to chemical analysis are those obtained by long treatment with hot mineral acids, among which the most common is hydrochloric.

It has long been assumed by soil analysts, perhaps not with justness, that such treatment removed from the soil, all those elements of plant food which could possibly be available for the needs of the growing crop. In this connection, however, the analyst must not forget that nature, in a series of years, with her own methods may easily accomplish what he in five days, even with the help of a hot mineral acid, may not be able to secure. Since, however, this method of solution has been so long practiced it is not the place here to throw doubt on its effectiveness without being able to suggest a better way. Of the mineral acids available no one possesses solvent powers for soils in a higher degree than hydrochloric. A somewhat detailed description will therefore be given of the methods of its use.

370. Strength of Acid to be Employed.—The fact that hydro-

[67] Journal of the Chemical Society, Transactions, 1902, **81** : 117.

[68] Journal of the Chemical Society, Transactions, 1905, **87** : 43.

chloric acid of nearly constant strength; *viz.*, specific gravity 1.115, equivalent to 22.9 per cent hydrochloric acid, may be obtained by distillation, led Owen to use acid of this density in his classic work on soil analysis. Hilgard has lately reviewed the conditions of constant strength in the solvent with results confirming the statements of Owen[69]. He evaporated on a steam-bath, to one-half its bulk, 50 cubic centimeters of hydrochloric acid, specific gravity 1.116, obtained by using the distillate from a stronger acid after rejecting the first third. The same operation was conducted with similar acid diluted with 10 per cent of water. The acid used contained 22.96 per cent hydrochloric acid. The residual acid contained 21.49 per cent hydrochloric acid. These results lead Hilgard to believe that the changes arising from evaporation in hydrochloric acid during soil digestion are insignificant, compared with those due to its action on the soluble matters, and that evaporation during digestion is effective in maintaining a definite strength in the solvent. For this reason it is contended that evaporation in a porcelain beaker covered by a watch-glass is more effective in constancy of conditions than digestion in a closed flask under pressure.

371. **Influence of Time of Digestion and Strength of Acid.**— Loughridge has made an interesting study of the influence of the strength of acid and time of digestion on the solution of soils.[70] The method of preparing the soil for the determination of the above points is as follows:

The soil, having been passed through the appropriate number of sieves to obtain the fine earth is pulverized with a wooden pestle and thoroughly mixed. The hygroscopic moisture is determined, after exposing it in a place saturated with vapor, in a layer not exceeding one millimeter in thickness for 12 hours, and subsequently drying at 200° in a paraffin-bath. Of this dried substance from two to three grams are used in the general analysis, the methods employed being in general those adopted by Peter.[71]

The quantities of materials dissolved by acids of different densities are shown below. The determinations are made by methods hereafter to be described.

[69] Agricultural Science, 1894, **8** : 1, et seq.

[70] American Journal of Science and Arts, 1874, [3], **7** : 20, et seq.

[71] Geological Survey in Kentucky, 1857. **8** : 177 et seq.

Ingredients.	Specific gravity of acid.		
	1.10	1.115	1.160
Insoluble residue	71.88	70.53	74.15
Soluble silica	11.38	12.30	9.42
Potash	0.60	0.63	0.48
Soda	0.13	0.09	0.35
Lime	0.27	0.27	0.23
Magnesia	0.45	0.45	0.45
Manganese oxid	0.06	0.06	0.06
Ferric oxid	5.15	5.11	5.04
Alumina	6.84	8.09	6.22
Sulfuric acid	0.02	0.02	0.02
Volatile matter	3.14	3.14	3.14
Total	99.92	100.69	99.56
Amount of soluble matter	24.00	27.02	22.27
" " " bases	13.50	14.70	12.83

From the above table it is seen that the strongest acid exerts the least soluble effect upon the substances present in the soil, while the greatest degree of solution was obtained by the acid of 1.115 specific gravity. This result indicates that while lime and magnesia are probably present chiefly as carbonates, potash as well as alumina, and to some extent lime, are present as silicates, and for that reason are not as fully extracted by acid of low strength as by that of medium concentration.

In regard to the influence of the time of digestion, the acid of specific gravity 1.115 being used, the data obtained are given in the following table:

Ingredients.	Number of days digested.				
	1.	3.	4.	5.	10.
Insoluble residue	76.97	72.66	71.86	70.53	71.79
Soluble silica	8.60	11.18	11.64	12.30	10.94
Potash	0.35	0.44	0.57	0.63	0.62
Soda	0.06	0.06	0.03	0.09	0.28
Lime	0.26	0.29	0.28	0.27	0.27
Magnesia	0.42	0.44	0.47	0.45	0.44
Manganese oxid	0.04	0.06	0.06	0.06	0.06
Ferric oxid	4.77	5.01	5.43	5.11	4.85
Alumina	5.15	7.38	7.07	7.88	7.16
Phosphoric acid	....	...	....	0.21	0.21
Sulfuric acid	0.02	0.02	0.02	0.02	0.02
Volatile matter	3.14	3.14	3.14	3.14	3.14
Total	99.78	100.68	100.57	100.69	99.78
Amount of soluble matter	19.67	24.88	25.57	27.02	24.85
" " " bases.	11.05	13.68	13.91	14.49	13.68

From this table it appears that the amount of dissolved ingredients increases up to the fifth day, the increase becoming, however, very slow as that limit is approached. It is also found that the ingredients offering the greatest resistance to this action are the same as those whose amounts were sensibly affected by the strength of the acid; namely, silica, potash, and alumina.

In regard to lime and magnesia, one day's digestion not being sufficient for full extraction, it is evident that they do not exist in the soil as carbonates or hydrated oxids only, as has been supposed, but also as silicates. A comparison of the results of the five and ten days' digestion shows that the solvent action of the acid has substantially ceased at the end of five days, there being no further increase of the amount of dissolved matter. In fact, some of the silica soluble after five days appears to become insoluble on further digestion.

372. **Digestion Vessels.**—Hilgard prescribes that the digestion of the sample of soil with acid be conducted in a small porcelain beaker covered with a watch-glass.[72] Kedzie, however, prefers beakers of bohemian glass, and shows as Fresenius also affirms that hydrochloric acid attacks the porcelain with greater energy than the glass.[73] Platinum would be the ideal material for the digestive vessels, but its great cost would exclude its general use for commercial work. In most cases it will be found that the error introduced into the analysis by the use of porcelain or bohemian glass beakers is quite small and not likely to affect the quantitative estimation of valuable soluble soil ingredients to any extent, except soda and potash.

In the laboratory of the Bureau of Chemistry some comparative tests made by Bigelow have shown that vessels of hard glass of special manufacture are less soluble in hot hydrochloric acid of 1.115 specific gravity than porcelain, thus confirming the observation of Kedzie. Following are the data showing the weights of material dissolved in 50 hours:

	Milligrams.
Berlin porcelain	2.8
Bohemian glass	1.7
Kaehler and Martini glass	1.2

[72] Bulletin 38, Division of Chemistry : 77.

[73] Bulletin 38, Division of Chemistry : 83.

In each case 25 cubic centimeters of the acid were used. The vessels all had approximately a capacity of 200 cubic centimeters.

373. **Processes Employed.—Hilgard's Method.**—The sample of soil sifted through a 0.5 millimeter mesh sieve and thoroughly air-dried, is conveniently preserved in weighing tubes. The actual content of hygroscopic and combined moisture may be previously made on a separate sample of soil.

In determining the amount of material to be employed for the general analysis regard must be had to the nature of the soil. This is necessary because of the impracticability of handling successfully such large precipitates of alumina as would result from the employment of as much as five grams in the case of calcareous clay soils; while in the case of very sandy soils even that quantity might require to be doubled in order to obtain weighable amounts of certain ingredients. For soils in which the insoluble portion ranges from 60 to 80 per cent, from two and a half to three grams is about the right measure for general analysis, while for the phosphoric acid determination not less than three grams should be employed in any case. It has been alleged that larger quantities must be taken for analysis in order to secure concordant results. It is difficult to see why this should be true for soils and not for ores, in which the results affect directly the money value, while in the case of soils the interpretation of results allows much wider limits in the percentages. Correct sampling must be presupposed to make any analysis useful; but with modern balances and methods it is difficult to see why five grams should be employed instead of half that amount, which in some cases is still too much for convenient manipulation of certain precipitates.

The desired quantity, usually from two to two and a half grams is brought into a small porcelain beaker, covered with a watch-glass, treated with from eight to ten times its bulk of hydrochloric acid of 1.115 specific gravity, and two or three drops of nitric acid, and digested for five days over the laboratory steam-bath. At the end of this time it is evaporated to dryness, first on the water-bath and then on the sand-bath. By this treatment all the silica set free is rendered insoluble.

374. Method of the Official Agricultural Chemists.—Place ten grams of the air-dried soil in a 150 to 200 cubic centimeter erlenmeyer flask, add 100 cubic centimeters of pure hydrochloric acid of specific gravity 1.115, insert the stopper with a long condensing tube, place in a steam-bath, and digest for ten hours at the temperature of boiling water, shaking once each hour. Pour the clear liquid into a small beaker, wash the residue out of the flask with distilled water onto a filter, and add the washings to the contents of the beaker. The residue is the amount insoluble in hydrochloric acid. Add a few drops of nitric acid to the filtrate to oxidize organic matter, and evaporate to dryness on the water-bath; take up with hot water and a few cubic centimeters of hydrochloric acid, and again evaporate to complete dryness. Take up as before, filter and wash thoroughly with cold water or with hot water slightly acidified at first with hydrochloric acid. Cool and make up to 500 cubic centimeters. This is solution A. The residue is to be added to the main residue and the whole ignited and weighed as insoluble matter.

Bigelow found in comparison made in the laboratory of the Bureau of Chemistry that digestion in flasks covered only with a watch-glass gives a larger quantity of dissolved matter in five days than the digestion under pressure does in 36 hours. The respective quantities of soluble and insoluble matter obtained by the two methods in two soils are as follows:

	Soil No. 1. Per cent.		Soil No. 2. Per cent.	
Method of digestion.	Insoluble.	Soluble.	Insoluble.	Soluble.
Open flask	75.62	24.38	79.62	20.38
Closed flask	76.81	23.19	80.48	19.52

375. Digestion with Continuous Agitation and at Constant Temperature.—The temperature at which a solvent acts on a soil has an important bearing on the quantity of material which passes into solution. The persistance of agitation also affects the progress of solution in a notable way.

An apparatus adapted by the author from Wagner's device for treating phosphatic slags and shown in figure 80 is used.

The apparatus is constructed of galvanized iron and as originally made, has double walls with half inch air space between

them. Where digestions are to be made at temperatures only slightly above that of the laboratory a cheaper form,[74] devised by Moore, with single walls answers every purpose.

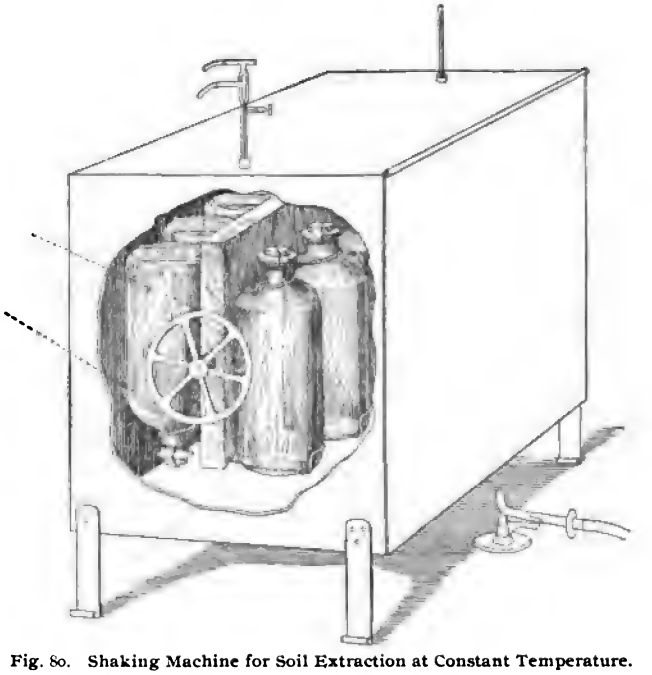

Fig. 80. Shaking Machine for Soil Extraction at Constant Temperature.

In the figure the end of the box is cut away to show the revolving board to which the digestion bottles are attached. These bottles are of about two liters capacity, closed when ready for use by rubber stoppers tied in. A convenient size of digester carries six bottles on each side arranged as shown in the figure. A thermometer at one end registers the temperature and a thermostat at the other controls the flame of the lamp.

By the use of this apparatus it is possible to have a uniform agitation and temperature throughout the work. The machine may be run by any motive power at hand at any convenient speed.

376. Digestion with Two-Hundredth Normal Hydrochloric Acid.—In order to determine approximately the quantities of potash

[74] Journal of the American Chemical Society, 1902, **24** : 82.

and phosphoric acid in a soil immediately available for an oat crop Moore has developed a method of treatment with dilute hydrochloric acid of $\frac{N}{200}$ strength.[75]

The apparatus described in the foregoing paragraph is used and the temperature is kept constantly at 40°. Several years after this apparatus had been in use in the Bureau of Chemistry Passon independently suggested its use.[76]

In order to determine the relation between crop feeding and the solubility of potash and phosphoric acid in the soils a long series of comparisons extending over several years was conducted. The method of digestion finally adopted requires the hydrochloric acid strength to be two-hundredth normal, after the neutralization of carbonates and basic principles, with constant agitation during a period of five hours.

In order to determine the basicity of the sample a preliminary digestion is conducted as follows: Twenty grams of the sample are digested with 100 cubic centimeters of tenth-normal hydrochloric acid for five hours at 40° with constant shaking, the digested mass brought onto a filter and ten cubic centimeters of the clear filtrate titrated with tenth normal alkali using methyl orange as indicator. If nine cubic centimeters of the alkali solution are required to secure neutrality it is evident that one-tenth of the acid used was required to decompose carbonates and neutralize basic matters in the soil. By means of a simple calculation, therefore, the quantity of x strength of acid necessary to produce a filtrate of a normal strength after digestion is ascertained.

It is convenient in each case to use tenth normal acid for preparing the solutions for all digestions of a less acid strength. In cases where the digestion bottles are made to hold one liter, as in those used in the Bureau of Chemistry, the quantity of dry soil used is conveniently made 186 grams. This quantity of soil of usual density placed in a container marked at one liter and which is filled with acid in the following manner. The quantity of tenth

[75] Journal of the American Chemical Society, 1902, **24** : 79 et seq.

[76] Zeitschrift für angewandte Chemie, 1898, **11** : 77, and Die landwirtschaftlichen Versuchs-Stationen, 1901, **55** : 25.

normal hydrochloric acid required to give a filtrate of two-hundredth normal strength after digestion with a given sample of soil is poured into the flask containing the sample and sufficient water added to fill the bottle half full. After thorough shaking the bottle is filled to the mark, stoppered as described and placed in the apparatus designed to secure the digestion with constant agitation at a given temperature. The traces of substances dissolved from the glass are of no consequence in soil analysis, excepting lime and potash. Blank experiments are made to determine the quantities of these bodies dissolved which are usually so small as to be of no consequence for practical purposes.

377. **The German Station Method.**—The method recommended by the German Stations[77] is greatly different from that described above both in temperature and time of digestion. To one part of the soil are added two parts by volume of a 25 per cent hydrochloric acid solution, the quantity being increased to correspond to any excess of carbonates. The mixture is left for 48 hours with frequent shaking. As an alternate method, one part of soil is treated with two parts by volume of ten per cent hydrochloric acid, and heated on the water-bath, with frequent shaking, for three hours.

The soluble materials are determined in the filtrate by some of the methods usually employed.

378. **The Belgian Method.**—The method of making the acid extract of the soil at the Gembloux Station does not differ greatly from some of those already described.[78]

The quantity of air-dried material taken is such that it may weigh exactly 300 grams exclusive of the moisture which it contains. It is dried at 150° for at least six hours. The drying is necessary in order to obtain an extract in hydrochloric acid of exactly 1.18 specific gravity. The dry earth is placed in a flask of two or three liters capacity to which one liter of hydrochloric acid of 1.18 specific gravity is added, being careful to take precautions to prevent frothing if much carbonate be present. The acid is allowed to act for 24 hours, it being frequently shaken

[77] Die landwirtschaftlichen Versuchs-Stationen, 1891, **38** : 311.

[78] Petermann, L'Analyse du Sol : 17.

meanwhile. After settling it is decanted and filtered upon a double-folded filter, the apex of which rests upon a small funnel covered with a plain filter of strong paper. Five hundred cubic centimeters of the filtrate are taken for the estimation, and in this filtrate are estimated the silica, phosphoric and sulfuric acids, potash, soda, iron, alumina, lime, and magnesia.

The filtrate is evaporated to dryness in a porcelain capsule, a few drops of nitric acid being added from time to time, and the liquid kept well stirred. The residue should be taken up with water, and if not perfectly free of organic matter, a second and even a third evaporation with nitric acid should take place, until all the organic matter is destroyed, which will be indicated by the clear yellow or reddish-yellow color of the liquid, caused by the iron oxid. After the last evaporation the material is dried in a drying oven one hour at 110°. The changes which take place in the solubility of the constituents of a soil when heated to 150° will be noticed hereafter. By reason of these changes in the soil the method of Petermann is open to grave objections.

379. **Treatment with Cold Hydrochloric Acid.**—According to the digestion method of Wolff[79] the soil sample is treated with cold concentrated hydrochloric acid. The process is as follows:

Four hundred and fifty grams of the soil dried at 100° are placed in a glass flask and treated with 1,500 cubic centimeters of hydrochloric acid of 1.15 specific gravity, corresponding to 30 per cent of gaseous hydrochloric acid. For every five per cent of calcium carbonate which the soil may contain, an additional 50 cubic centimeters of hydrochloric acid are added. With frequent stirring, the soil is left in contact with the acid for 48 hours and then 1,000 cubic centimeters of liquid, as clear as possible, are poured off, which corresponds to 300 grams of the soil. After dilution with water it is filtered and the filtrate treated with a few drops of nitric acid and evaporated to dryness to destroy organic matter and render the dissolved silica insoluble. After the separation of the silica the solution is again made up with water to 1,000 cubic centimeters.

Two hundred cubic centimeters of this solution, corresponding

[79] Zeitschrift für analytische Chemie, **8** : 92.

to 60 grams of the soil, are used for the estimation of iron, alumina, lime, manganese, and magnesia.

Four hundred cubic centimeters of the solution, corresponding to 120 grams of the soil, are left for the estimation of sulfuric acid and alkalies. This method gives from five to six times less alkalies and a much smaller quantity of iron than the treatment with hot acid. In the use of hot acid, therefore, Wolff reduces the quantity of soil acted on to 150 grams.

380. Treatment with Nitric Acid.—For the purpose of estimating phosphoric acid Grandeau[80] directs that the soil be extracted with nitric acid. For this purpose 25 grams of the air-dried fine earth are placed in a porcelain dish covered with a watch-glass, and treated cautiously with nitric acid in small quantities at a time. If the soil be calcareous in its nature it should be previously moistened with water, and the acid so added as to avoid undue effervescence. Sufficient acid is added to strongly saturate the sample and it is then digested on the sand-bath for two hours; or at least until the organic matters are destroyed, which will be indicated by the cessation of evolution of nitrous vapors. The evaporation is carried to dryness, (removing the cover), the residue taken up with water and dilute nitric acid, digested for half an hour, filtered into a 500 cc. flask, and worked up to the mark.

381. Digestion with Hydrofluoric and Sulfuric Acids.—When a complete disintegration of the siliceous substances in soils is desired as in analysis in bulk, the decomposition is easily accomplished by digestion with the above named acids in a platinum dish. The fine earth is saturated with a concentrated aqueous solution of hydrofluoric acid to which a few drops of sulfuric acid are added. It is then digested until nearly dry. If any undecomposed particles remain, the treatment is continued until complete decomposition is secured. The silica is thus all volatilized as hydrofluosilicic acid and the bases pre-existing in the soil are left as sulfates. This method of treatment is especially recommended when it is desired to estimate the whole quantity of any of the soil constituents with the exception of silica. The silica may, however, be determined in the distillate. Instead of using the solution

[80] Traité d'Analyse des Matiéres agricoles, 3rd edition, 1 : 144.

of hydrofluoric acid, ammonium fluorid may be employed. In this process the sample of earth reduced to an impalpable powder by grinding in an agate mortar is mixed with four or five times its weight of the ammonium fluorid in a platinum dish and thoroughly moistened with sulfuric acid and allowed to stand at room temperature for several hours. It is then gently heated until all fumes of hydrofluosilicic acid have been driven off, but is not raised to a red heat. If any undecomposed particles remain, the above treatment is repeated.

382. **Summary.**—In the various methods which have been described for the treatment of soils with solvents it is evident that in most cases the processes are conventional. It is only when complete solution is secured, as for instance with hydrofluoric acid, that definite results are reached. Next in order of definiteness is the process recommended by Hilgard where the data show in so far as they have been tabulated and compared, that evaporation in an unconfined space with hydrochloric acid of 1.115 specific gravity establishes a permanent state of acid strength and reaches at about the temperature of boiling water, a definite degree of solution in about five days. If a continuous agitation should be practiced with this method, as is the case with the digestion process with dilute hydrochloric acid as secured in Moore's method, the time of reaching equilibrium might be materially shortened.

In all the cases where the solvent is a weak mineral acid, an organic acid, carbonic acid, salts or water, it is evident that no condition of equilibrium can be secured within the time ordinarily at the disposition of practical analysts. With such solvents time, temperature and continuity of agitation are dominant factors, which are to be carefully considered when concordant results are to be obtained. The important influence of these factors is fully set forth in the data from the Bureau of Chemistry already cited. The strength of the acid employed and the influence of basic substances and carbonates in diminishing the strength of the solvent have also been pointed out.

For practical purposes and for the sake of comparison the official method of securing the ingredients in a soil soluble in a reasonable time in hot hydrochloric acid is recommended. In this

case, since the degree of solution is not definite the terms of the convention should be rigidly adhered to by all analysts using the process. The data secured by this process, as well as those obtained by Hilgard's, represent the total plant food, with the exception of nitrogen, in a soil which is likely to become available in a large number of years. On the contrary, the data secured by the action of weak solvents at comparatively low temperature represent more nearly the quantities of plant food which the crops of the immediate future shall find at their disposal. Finally the total content of the plant foods in the soil, with the exception of nitrogen, is revealed by the solution of the whole mineral mass, composed as it is chiefly of silica in some form of hydrofluoric acid.

DETERMINATION OF THE QUANTITY AND CHARACTER OF DISSOLVED MATTER.

383. **Substances in Solution.**—By treatment with solvents as indicated in the preceding paragraphs, greater or less quantities of the original constituents of soil are brought into solution. The total quantity of dissolved matters is determined by drying and weighing the insoluble residue and the percentages of soluble and insoluble matters should be noted; and each portion saved for further examination. In this country the common practice of soil analysis is to digest the sample with hydrochloric acid. The following paragraphs, therefore, will be devoted to the general methods of determining the matters dissolved by that treatment, leaving for later consideration the special methods of analysis. The fundamental principle on which the treatment with hydrochloric acid rests is based on the belief that such treatment practically extracts from the soil all those elements which are likely to become, immediately or in the near future, available for plant food.

384. **Hilgard's Methods.**[81]—(1) *Removal of Soluble Silica.*—The acid filtrate obtained by the process given in paragraph 373 is employed for the following determinations. After the solution obtained has been evaporated to dryness to render silica insoluble, it is moistened with strong hydrochloric acid and two or three drops of nitric acid. The mass is warmed, and after allowing to

[81] Bulletin 38, Division of Chemistry : 77.

stand for a few hours on a steam-bath is taken up with distilled water. After clearing, it is filtered from the insoluble residue, which is strongly ignited and weighed. If the filtrate should be turbid the insoluble residue which has gone through the filter can be recovered in the iron and alumina determination.

The insoluble residue is next boiled for 15 or 20 minutes in a concentrated solution of sodium carbonate, to which a few drops of caustic lye should then be added to prevent reprecipitation of the dissolved silica. The solution must be filtered hot. The difference between the weight of the total residue and that of undissolved sand and mineral powder is recorded as soluble silica, being the aggregate of that set free by the acid treatment and that previously existing in the soil. The latter, however, rarely reaches five per cent.

(2) *Destruction of Organic Matter.*—The acid filtrate from the total insoluble residue is evaporated to a convenient bulk. In case the filtrate should indicate by its color, the presence of any organic matter, it should be oxidized by aqua regia, otherwise there will be difficulty in separating alumina.

(3) *Precipitation of Iron and Alumina.*—The filtrate thus prepared is now brought to boiling and treated sparingly with ammonia, whereby iron and alumina are precipitated, together with any phosphoric acid which may be present if not in excess of quantity necessary to combine with the two bases mentioned. It is kept boiling until the excess of ammonia is driven off, and then filtered hot. (Filtrate A). The previous addition of ammonium chlorid is usually unnecessary. If the boiling is continued too long, filtration becomes very difficult and a part of the precipitate may redissolve in washing. Filtration may be begun as soon as the nose fails to note the presence of free ammonia; test paper is too delicate. Failure to boil long enough involves the contamination of the iron-alumina precipitate with lime and manganese.

(4) *Estimation of Iron and Alumina.*—The iron and alumina precipitate with filter of (3) is dissolved in a mixture of about five cubic centimeters of hydrochloric acid and 20 cubic centimeters of water, filtered and made up to 150 cubic centimeters.

In 50 cubic centimeters determine the iron and alumina together by precipitation with ammonia, after oxidizing the organic matter (in the filter from 3) with aqua regia. Fifty cubic centimeters of the solution are used for iron alone and 50 cubic centimeters are kept in reserve. Determine the iron by means of a standard solution of potassium permanganate after reduction, which is accomplished by evaporating the 50 cubic centimeters almost to dryness with strong sulfuric acid, adding water and transferring the solution to a flask, and then reducing by means of pure metallic zinc in the usual way. The alumina and phosphoric acid are then calculated by difference and the latter determined as described further on deducted to get the weight of alumina. This method of determining the two oxids in their intermixture is in several respects more satisfactory than the separation with caustic alkalies, which, however, has served for most determinations made, until within the last ten years. It is, however, much more liable to miscarry in unpracticed hands than the other.

(5) *Estimation of Lime.*—The filtrate A from the iron and alumina is acidified slightly with hydrochloric acid, and if too bulky is evaporated to about 25 cubic centimeters, unless the soil is a very calcareous one, and the lime is precipitated from it by neutralizing with ammonia and adding ammonium oxalate. The precipitation of the lime should be done in the hot solution, as the precipitate settles much more easily. It is allowed to stand for 12 hours, then filtered (filtrate B), washed with cold water, and dried. By ignition the lime precipitate is partially converted into the oxid. It is then heated with excess of powdered ammonium carbonate, moistened with water, and exposed to a gentle heat (50°-80°) until all the ammonia is expelled. It is then dried below red heat and weighed as calcium carbonate. When the amount of lime is at all considerable, the treatment with ammonium carbonate must be repeated till a constant weight is obtained.

(6) *Estimation of Sulfuric Acid.*—The filtrate B from the calcium oxalate is put into a hard bohemian flask, boiled down over the sand-bath, and the ammoniacal salts destroyed with aqua regia. From the flask it is removed to a small beaker and evaporated to dryness with excess of nitric acid. This process usually

occupies from four to five hours. The residue should be crystalline-granular. If it is white-opaque, ammonium nitrate remains and must be destroyed by hydrochloric acid. The dry residue is moistened with nitric acid, and the floccules of silica usually present separated by filtration from the filtrate, which should not amount to more than 10 or 15 cubic centimeters. The sulfuric acid is precipitated by treatment with a few drops of barium nitrate, both the solution and the reagent being heated to boiling. If the quantity of sulfuric acid is large it may be filtered after the lapse of four or five hours (filtrate C), if very small it should stand 12 hours before filtering. The precipitate is washed with boiling water, dried, ignited, and weighed. Care should be taken in adding the barium nitrate to use only the least possible excess, because in such a small concentrated acid solution the excess of barium nitrate may crystallize and will not again readily dissolve in hot water. Care must also be taken not to leave in the beaker the large heavy crystals of barium sulfate, of which a few sometimes constitute the entire precipitate, rarely exceeding a few milligrams. Should the ignited precipitate show an alkaline reaction on moistening with water, it must be treated with a drop of hydrochloric acid, refiltered and weighed. The use of barium acetate involves unnecessary trouble in this determination.

(7) *Estimation of Sodium and Potassium.*—Filtrate C is now evaporated to dryness in a platinum dish, the residue is treated with an excess of crystallized oxalic acid, moistened with water, and exposed to gentle heat. It is then strongly ignited to change the oxalates to carbonates. This treatment with oxalic acid must be made in a vessel which can be kept well covered, otherwise there is danger of loss through spattering. As little water as possible should be used, as otherwise loss from evolution of carbon dioxid is difficult to avoid. Spatters on the cover should not be washed back into the basin until after the excess of oxalic acid has been volatilized. The ignited mass should have a slightly blackish tinge which shows the conversion of the nitrates into carbonates. White portions may be locally retreated with oxalic acid. The ignited mass is treated with a small amount of water, which dissolves the alkaline carbonates and leaves the magnesium carbonate, manganese protosesquioxid, and the excess of barium carbon-

ate behind. The alkalies are separated by filtration into a small platinum dish (filtrate D), and the residue is well but sparingly washed with water on a small filter. When the filtrate exceeds ten cubic centimeters it may, on evaporation, show so much turbidity from dissolved earthy carbonates as to render refiltration on a small filter necessary, since otherwise the soda percentage will be found too large and magnesia too small. If, on dissolving the ignited mass, the solution should appear greenish from the formation of alkaline manganates, add a few drops of alcohol to reduce the manganese to insoluble dioxid.

The filtrate D, which should not be more than 10 or 15 cubic centimeters, containing the carbonates of the alkalies, is evaporated to dryness and gently fused, so as to render insoluble any magnesium carbonate that may have gone through; then redissolved and filtered into a small weighed platinum dish containing a few drops of dilute hydrochloric acid, to change the carbonates into chlorids, evaporated to dryness, and exposed to a gradually rising temperature (below red heat), by which the chlorids are thoroughly dried and freed from moisture, so as to prevent the decrepitation that would otherwise occur on ignition. Holding the platinum basin firmly by forceps grasping the clean edge, pass it carefully over a very low bunsen flame, so as to cause, successively, every portion of the scaly or powdery residue to collapse, without fully fusing. There is thus no loss from volatilization, and no difficulty in obtaining an accurate, constant weight. The weighed chlorids are washed by means of a little water into a small beaker or porcelain dish, treated with a sufficient quantity of platinum chlorid, and evaporated to dryness over the water-bath. The dried residue is treated with a mixture of three parts absolute alcohol and one part ether, which does not dissolve the potassium platinochlorid. This is brought on a filter, and washed with ether-alcohol. When dry, the precipitate and filter are put into a small platinum crucible and exposed to a heat sufficiently intense to reduce the platinum chlorid to metallic platinum and to volatilize the greater part of the potassium chlorid. This is easily accomplished in a small crucible, which is roughened by being constantly used for the same purpose (and no other), the spongy metal causing a ready evolution of the gases. The reduced plat-

inum is now first washed in the crucible with hot acidulated water, then with pure water, then all moisture is driven off and it is weighed. From the weight of the platinum, is calculated the potassium chlorid and the oxid corresponding; the difference between the weights of the total alkaline chlorids and potassium chlorid gives the sodium chlorid, from which may be calculated the sodium oxid. When the heating of the platinum precipitate has not been sufficient in time or intensity, instead of being in a solid spongy mass of the color of the crucible itself, small black particles of metallic platinum will obstinately float on the surface of the water in the crucible, and it becomes difficult to wash without loss.

(8) *Estimation of Manganese.*—The residue of barium, magnesium, and manganese compounds is treated on the filter with hydrochloric acid, and the platinum dish is washed with warm nitric acid (not hydrochloric, for the platinum dish may be attacked by chlorin from the manganese oxid) dissolving any small traces of precipitate that may have been left behind. The solution containing the magnesium and manganese chlorids is freed from barium salts by hot precipitation with sulfuric acid, and the barium sulfate, after settling a few hours, is separated by filtration. The filtrate is neutralized with ammonia, any resulting small precipitate (of iron) is filtered, and the manganese precipitated with ammonium sulfid, let stand 12 hours, filtered (filtrate E); washed with cold water, dried, ignited, and weighed as manganese protosesquioxid, Mn_3O_4. If preferred the manganese may be precipitated with chlorin or bromin water as dioxid, but the process requires a rather longer time and may fail in inexpert hands more readily than the method given.

(9) *Estimation of Magnesium.*—The filtrate E from the manganese is now freed from sulfur by acidulating with hydrochloric acid, evaporating, if necessary, and filtering. From the filtrate the magnesia is precipitated by adding an equal bulk of ammonia water and then sodium phosphate. After standing at least 24 hours, the magnesium salt may be filtered, washed with ammoniacal water, dried, ignited, and weighed as magnesium pyrophosphate.

385. Examination of Acid Extract by the Methods of Petermann.—*Estimation of the Silica.*—The Gembloux method of estimating silica consists in taking up the dry extract obtained from the treatment of the soil, in the manner described in paragraph **378**, with water and a few drops of hydrochloric acid, heating for a short time on a sand-bath to facilitate the solution, and filtering, washing, drying, igniting, and weighing the residue obtained as silica.

Estimation of the Sulfuric Acid.—The filtrate obtained in the estimation of silica is heated for half an hour with a few drops of nitric acid and the volume made up to 500 cubic centimeters. One hundred cubic centimeters of this are precipitated with barium chlorid, diluted to double its volume, heated for some time, the precipitate of barium sulfate collected and weighed, and the quantity of sulfuric acid calculated therefrom.

Potash and Soda.—Potash and soda are estimated by heating the filtrate obtained in the estimation of the sulfuric acid and precipitating the excess of barium in the hot solution after the addition of ammonia by ammonium oxalate and carbonate. The whole is allowed to digest for six hours at a gentle heat and then allowed to remain at rest for 24 hours, filtered, washed, and the filtrate evaporated to dryness in a large platinum dish and the ammoniacal salts driven off at a low temperature. At the end the temperature is carried a little higher until it reaches low redness. The residue is taken up by distilled water, filtered into a weighed platinum dish, a few drops of hydrochloric acid added, evaporated, dried, heated with great care and the sodium and potassium chlorids obtained weighed together. The respective quantities of potash and soda are estimated in the usual way by precipitating the potash with platinum chlorid, and deducting the weight of potassium obtained as chlorid from the total weight of the double chlorids.

Estimation of the Iron and Aluminum Oxids.—The iron and aluminum oxids are estimated in 25 cubic centimeters of the primitive solution obtained with hydrochloric acid after removal of soluble silica by adding ammonium carbonate almost to complete neutralization, that is to say until the pre-

cipitate formed is just redissolved in the feeble excess of hydrochloric acid which remains, and the liquid changes from a clear red to a blood red tint. Dilute with distilled water and precipitate with a little excess of ammonium acetate, and boil until, after interrupting the boiling for a moment, the basic iron and aluminum acetate and the small quantity of iron and aluminum phosphate present are easily deposited, and the supernatant liquid is limpid and colorless. Wash the precipitate by decantation, boiling each time, filter, wash the filter with boiling water to which a little ammonium acetate has been added, dry, ignite, and weigh. The material obtained consists of ferric oxid, aluminum oxid, and iron and aluminum phosphates. Deduct from the whole, the phosphoric acid determined in another portion. The residue will be the sum of the iron and aluminum oxids.

Estimation of the Lime.—The filtrate from the portion used for the estimation of the iron and alumina, which has a feeble reaction due to acetic acid, is treated hot with ammonium oxalate. The mixture is kept at a gentle heat for at least twelve hours, after which it is filtered, washed with hot water, dried, and ignited over a blast-lamp to constant weight and weighed as calcium oxid.

Estimation of the Magnesia.—For the estimation of the magnesia the filtrate obtained in the estimation of lime is evaporated to dryness in a platinum dish, the ammoniacal salts driven off, the residue taken up with water slightly acidified with hydrochloric acid, filtered, the filtrate made strongly alkaline with ammonia and heated some time to the boiling point to precipitate any traces of iron and alumina which may have remained in solution. Filter, wash, allow to cool and precipitate the magnesia with constant shaking or stirring by the addition of sodium phosphate, allow to stand for 12 hours, collect on a filter, ignite, and weigh as pyrophosphate, and calculate the quantity of magnesia from the weight of salt obtained.

Estimation of the Phosphoric Acid.—The phosphoric acid is estimated in 100 cubic centimeters of the original solution obtained by the treatment of the soil with hydrochloric acid by removing the silica and again evaporating it to dryness on the water-bath. The residue is taken up with water to which a few

drops of nitric acid have been added and filtered. The total phosphoric acid is then obtained by precipitation with ammonium molybdate in the usual way.

386. Analysis of the Insoluble Residue.—The insoluble residue left after digestion with hydrochloric acid is not without interest from an agricultural and analytical point of view. While it is true that the plant food, therein contained, is not immediately available, yet it must not be forgotten that the method of the chemist may not fix a limit to nature's method of collecting nutriment for plants. In however refractory a state they may exist, it is possible that all nutritive elements therein may eventually become available for assimilation. For the completion of an estimate of the total nutritive power of a soil, therefore a further examination of the insoluble residue should be made. The methods of securing this are essentially those of making a bulk analysis of the soil.

The principle of the method depends on the reduction of the sample to an impalpable powder and the subsequent decomposition of the insoluble portions by treatment with hydrofluoric and sulfuric acids or by fusion with the alkalies.

387. Method of Wolff for Treating Residue Insoluble in Hot Hydrochloric Acid.[82]—The well-washed residue is dried with the filter, then separated therefrom, the filter burned and the ash weighed with the whole of the residue. About eight grams of the residue are ignited and serve for the estimation of the insoluble mineral matter. Another portion of ten grams of the dried, but not ignited, residue is boiled with a concentrated solution of sodium carbonate with the addition of caustic soda, and the quantity of dissolved silicic acid estimated. A third portion of about 15 grams is treated with about five times its weight of pure concentrated sulfuric acid, and is evaporated until the mass has taken the form of a dry powder. After moistening with concentrated hydrochloric acid the mass is boiled with water, filtered, and the filtrate examined according to the ordinary methods for silicic acid, alumina, iron, lime, magnesia, and alkalies. The residue after treatment with concentrated sulfuric acid is dried, but not

[82] Zeitschrift für analytische Chemie, 1864, **3** : 98.

ignited, and boiled with a concentrated solution of sodium carbonate with the addition of a little caustic soda, filtered, heated, and the silicic acid separated from the solution. After thorough washing, the residue, after ignition, is weighed and represents the material insoluble in concentrated hydrochloric and sulfuric acids. The silicic acid found as before, together with the small quantity dissolved in the hydrochloric acid extract, gives, in connection with the alumina contained in the sulfuric acid extract, approximately the quantity of pure water-free clay contained in the soil.

In six samples of soils of very different compositions which were examined by the above process, it was found that the clay had the following mean composition: Silicic acid, 55.1 to 61.5 per cent, alumina, 38.6 to 44.9 per cent; as means 58.05 per cent silicic acid and 41.95 per cent alumina.

Finally, four or five grams of the residue, after treatment with sulfuric acid and sodium carbonate, are rubbed up in an agate mortar and completely separated into silt by water. The silt mass is dried, lightly ignited, and three grams of it spread in a flat platinum dish moistened with sulfuric acid, and subjected to the action of hydrofluoric acid in a lead oven at 60°, until a complete decomposition of the material is accomplished. In the solution all the different bases can be determined.

388. **Method of the Belgian Chemists.**—The method employed by Petermann[83] at the Gembloux Station in the examination of the part of the soil insoluble in hydrochloric acid consists in washing the insoluble portion by decantation with distilled water until all acid reaction is removed. Place the contents of the flask and of the filter in a porcelain dish and dry. After a careful mixing of the mass take out about 50 grams and wash upon a filter until all reaction for chlorin has disappeared, dry, detach the mass from the filter and incinerate. Place in a platinum crucible two grams of the ground and ignited residue and mix it, using a platinum stirring rod, with 12 grams of ammonium fluorid; heat slightly over a Bunsen burner in a muffle with a good draught and regulate the flame in such a way that the operation shall con-

[83] L'Analyse du Sol : 21.

tinue for about one hour. After complete decomposition add about two cubic centimeters of sulfuric acid in such a way as to completely saturate the residue, drive off the sulfuric acid carefully at a low red heat and take up the residue with water slightly acidulated with hydrochloric acid and wash the whole into a flask of 500 cubic centimeters capacity. Oxidize by heating for an hour with nitric acid, make up to the mark and filter. The percentages of potash, soda, lime, magnesia, and the silicates are determined exactly as in the hydrochloric acid extract. The decomposition of the silicates by ammonium fluorid has been compared by Petermann with the other standard methods of attack, *viz.:* by a solution of hydrofluoric acid, by the gaseous acid and by fusion with alkaline carbonates, and is preferred by him to all other methods. Some of these methods of decomposition require as much as three days time and introduce into the mass large quantities of substances, such as potash and soda, of which small quantities only exist in the sample to be analyzed. In many hundreds of analyses he has not found in any case that more than two hours were necessary to secure a complete decomposition of the sample with ammonium fluorid.

389. **Bulk Analysis.**—It is frequently desirable to determine the total composition of a soil sample as well as the nature of that part of it soluble in any of the solvents usually employed. To this end the methods of mineral analysis are employed. The variations which occur in duplicate analyses are probably due to the small quantities of material taken for analysis, it being difficult to obtain average samples of a material which is not very finely powdered when small quantities are used. Moreover, as it is likely to become of importance to know whether the proportions of lime and magnesia vary by as much as one-tenth per cent, and such small variations are within the limits of error of an analysis, and as the total proportion of lime and magnesia in highly siliceous soils, probably does not exceed one-tenth per cent, it is deemed best to take a large quantity of soil for the bulk analysis in each case. The amount adopted for the highly siliceous soils containing much quartz is ten grams. This quantity, taken after quartering down the entire sample, is ground to an

impalpable powder and used for the determination of the lime, magnesia, and alkalies, the silica, iron oxid, alumina, and loss on ignition, being determined in one gram samples. The ten grams are decomposed by hydrofluoric and sulfuric acids or by ammonium fluorid in a large platinum dish, the solution evaporated, at first on the water-bath until all water is removed, and then at a higher temperature until all the free sulfuric acid is driven off, when the residue is heated in a muffle at a low red heat for several hours. At this temperature the sulfuric acid combined with the iron oxid and alumina is driven off, leaving the remaining sulfates unchanged and the iron oxid and alumina are in the form of a powder of no great volume which is easily and quickly washed. This operation is usually successful at first but in some cases the decomposition is not complete as is shown by the appearance of a precipitate on adding ammonia to the filtrate from the aluminum and iron oxids. In such cases the precipitate is dissolved in hydrochloric acid, reprecipitated by ammonia and removed by filtration. In the filtrate from the thoroughly washed aluminum and iron oxids, lime is precipitated as oxalate and separated by filtration; the filtrate is evaporated to dryness and the ammonia salts driven off by heat; the magnesia in the unfiltered watery extract of this residue is precipitated by baryta water, which also removes the sulfuric acid with which the bases had been combined. In the filtrate from this precipitate baryta is precipitated by ammonium carbonate and removed by filtration, leaving the alkalies to be determined in the usual way after conversion into chlorids. The mixed precipitate of magnesia and barium sulfate is treated with hydrochloric acid, filtered, the baryta present removed as sulfate, and the magnesia precipitated in the filtrate from the latter as phosphate. The advantages of this method are that the large quantity of material employed gives some assurance that an average sample has been operated on, and all the bases present in small proportions are estimated in the same sample. The objection to it is the time consumed both in grinding the samples and in determining all the bases in one solution. As a small quantity of material is generally used for determining the silica, iron oxid, alumina, and loss by ignition, and a larger quantity for the remaining bases, slight differences in the unground sam-

ples are unavoidable, especially when the quartz grains are somewhat large, it being practically impossible to take two small samples of such a soil which would have the same number of quartz grains. Consequently tedious grinding of large quantities of the soils for the bulk analysis is necessary. This objection does not apply to the official analysis or assay of soils in which considerable quantities are extracted by acid and the solution analyzed, and silica is not determined. In any case, it may be said, when it becomes an object to know whether a soil contains a total of 0.1 or 0.2 per cent of lime or magnesia, of 0.7 or 0.5 per cent of potash, one analysis even of the large quantity of ten grams would be insufficient to decide the point, and at least the mean of two determinations should be taken. The phosphoric acid may be determined as described further on.

The details of modern methods of mineral analysis are fully described by Hillebrand.[84]

SPECIAL METHODS OF DETERMINATION OF SOIL CONSTITUENTS.

390. **Preliminary Considerations.**—In the foregoing paragraphs the general outline of the chemical methods of soil examination have been given. There are often occasions, however, which demand a special study of some particular soil constituent. It has been thought proper, therefore, to add here some of the best approved methods of special determinations which have been approved in this and other countries.

In the main, the final determination of any particular element of the soil, and its previous separation from accompanying elements, are based on the general processes already given. The variations in many instances, however, are of such importance as to require special mention.

391. **Condition of Potash in Soils.**—Potash exists in the soil in very different states. That part of it which is combined with the humus material, or with the hydrated silicates, is easily set free from its combinations and is to be regarded as the more assimilable portion.

The potash in the soil is found chiefly in combination with

[84] United States Geological Survey, Bulletin No. 176.

silicates, and particularly with the hydrated aluminum silicates, forming clay. As the particles with which it is combined are found in a state of greater or less fineness, the potash itself is set free under the influences of the agents which are active in the soil, with greater or less rapidity, passing into a form in which it can be utilized by plants. In silicates which are very finely divided, such as clay, the potash becomes active in a relatively short time, while in the débris of rocks in a less advanced state of decomposition it may rest for an indefinite period in an inert state. The estimation of the potash which is assimilable in the clay is more important for agricultural purposes than to determine that which may be present in the soil in firmer combination. Treating the sample of soil with water, especially if for a short time, does not furnish any reliable information in regard to the potash which the soil contains, nor of its agricultural relations. Indeed, the absorbing properties of the soil tend to prevent the elimination of the potash in this way, to a certain extent, even when it is found in the soluble state. It is therefore, necessary to employ some stronger solvent to set the potash free, but variable results are obtained, according to the employment of acids, or other active solvents of greater or less concentration and for longer or shorter periods of contact.

392. **French Official Methods for Potash.**—In the method of the French agricultural chemists[85], 20 grams of the earth are placed in a dish with a flat bottom, 11 centimeters in diameter, and rubbed up with from 20 to 30 cubic centimeters of water. There is added carefully, and in small quantities, some nitric acid of 36° Baumé until all effervescence has ceased, the mass meanwhile being thoroughly stirred. When the carbonates have been decomposed, which can be told by the cessation of the effervescence, 20 cubic centimeters more of the same acid are added. The dish is heated on the sand-bath for five hours, regulating the heating in such a way that there still remains some acid at the end of the operation and the mass is not thoroughly dry. The acid mass is then taken up with hot water, filtered, and washed with hot water until the amount of filtrate is about 300 cubic centimeters. The filtrate should be received in a flask of about one liter capac-

[85] Annales de la Science agronomique, 1891, **8** : 278.

ity. The filtrate will contain the dissolved potash, soda, magnesia, lime, iron and aluminum oxids, and traces of sulfuric and phosphoric acids. For the elimination of the other substances, with the exception of potash, soda, and magnesia, a few drops of barium nitrate are added, afterwards sufficient ammonia to render the solution alkaline, and finally an excess of ammonium carbonate in powder added in small portions. These materials are added successively and the whole is left to stand for 24 hours. By this operation the sulfuric acid is separated in the form of barium sulfate; the iron and aluminum oxids are precipitated, carrying down with them the phosphoric acid, and the lime is thrown down in the form of carbonate. The mass is filtered and washed several times with hot water. The filtrate contains in addition to potash, soda, magnesia, and the ammoniacal salts which have been introduced. The ammonium salts are destroyed by adding aqua regia and evaporating the liquid to a very small volume. The mass is evaporated in a porcelain dish of about seven centimeters diameter, with a flat bottom, and an excess of perchloric acid added. The evaporation is carried to dryness on a sand-bath, and the heating prolonged until the last white fumes of perchloric acid are disengaged. The mass is left to cool. There are added five cubic centimeters of alcohol, of 90° strength. The mass is triturated by a stirring rod, the extremity of which is flattened, in such a manner as to reduce it all to an impalpable powder. It is left to settle and the supernatant liquid is decanted upon a small filter. The treatment with alcohol of the kind, quantity, and strength described, is continued four or five times. Afterwards, as there may still remain a trace of the sodium and magnesium perchlorates in the interior of the crystals of potassium perchlorate, there are added to the capsule in which all of the alkaline residue has been collected, two or three cubic centimeters of water, and it is evaporated again to dryness and taken up twice with small quantities of alcohol. There are thus removed any traces of sodium and magnesium perchlorates which may have been occluded in the potassium perchlorate crystals. By means of a jet of boiling water the stirring rod and the filter, which contains the small quantities of potassium perchlorate, are washed, and the liquid passing through is received in the capsule

which contains the larger part of the salt. It is evaporated to dryness and weighed.

When there is very little magnesia present, as is generally the case, the estimation of the potash is made without any difficulty by the process just mentioned, but when the proportion of magnesia is high it is found useful to separate it before the transformation into perchlorates. The magnesia is separated by carbonating the residue as indicated in the method for the estimation of magnesia, by treatment with oxalic acid and ignition. By extracting the carbonates of the alkalies thus formed with very small quantities of water, and filtering, they are obtained free from magnesia.

It is advisable to test the purity of the potassium perchlorate formed which sometimes contains a little silica. For this purpose it is dissolved in boiling water, and any residue which remains is weighed, and that weight deducted from the total weight of perchlorate. By multiplying the weight of potassium perchlorate found by the coefficient 0.339, the quantity of potash contained in the 20 grams of soil submitted to analysis is obtained.

Estimation of the Potash Soluble in Cold, Dilute Acids.— (Method of Schlösing). Introduce 100 grams of the soil into a one or one and a half liter flask with from 600 to 800 cubic centimeters of water. A little nitric acid, of 30° Baumé, is added until the carbonate is decomposed and a slight acid reaction is obtained. Afterwards five cubic centimeters of the same acid are added and it is left to digest for six hours, shaking every 15 minutes. Instead of taking the whole of the wash-water for the examination, it is better to extract only a portion of it and so dispense with washing. This process is conducted in the following manner:

The weight P of the full flask having been determined, as much as possible of the solution, is decanted by means of a very small siphon, of which the flow is moderated by fixing a rubber tube with a pinch-cock to its lower extremity. After the decantation is complete, the flask is again weighed, giving the weight of P′; the weight of liquid taken, therefore, is equal to P — P′. To determine the total weight of the liquid, throw upon a filter the earthy residue insoluble in the acid, and after washing and drying it determine its weight *r*. The weight of the empty dry flask *p*

is also determined. The total weight of the soil will be, therefore, $P - r - p$. The part of the liquid which was extracted from the flask, and upon which the analytical operation is to be conducted is represented by the formula

$$\frac{P - P'}{P - r - p}.$$

This method avoids washing and evaporation which would be of very long duration. It rests upon the supposition that the solid matter from which the liquor is separated has no affinity for the dissolved substances, and that the total of these substances has passed into the liquor, and that the solution is homogeneous.

In the liquor first decanted as described before, the potash is to be estimated. This liquor contains in addition to potash, soda, lime, magnesia, iron and aluminum oxids, as well as phosphoric, sulfuric, and hydrochloric acids. There is first added to it a little barium chlorid to precipitate the sulfuric acid. It is heated to about 40° in a glass flask and some ammonium carbonate added in a solution containing an excess of ammonium hydroxid. By this process the lime, and the excess of baryta are precipitated in the form of carbonates, the alumina and iron as oxids, and the phosphoric acid in combination with the last two bases. The magnesium carbonate is not precipitated because it is soluble in the ammonium carbonate with which it forms a double salt.

The employment of a gentle heat favors the formation of the precipitate of calcium carbonate in a granular form which lends itself easily to filtration. The contents of the flask are thrown upon a filter and the insoluble residue washed. The filtrate contains the potash, soda, magnesia, ammonia, and nitric and hydrochloric acids. It is concentrated as rapidly as possible by heating in a flask, and afterwards the ammoniacal salts are destroyed by weak aqua regia and the whole is then transferred to a porcelain dish and evaporated to dryness. There is thus obtained a mixture of potassium, sodium, and magnesium nitrates, from which the potash is separated by means of perchloric acid in the manner already described.

Estimation of the Total Potash.—Beside the potash which can be dissolved by the boiling concentrated acids the soil contains

potash combined with silicates, which becomes useful for plant life with extreme slowness. It is often of great interest to estimate the total potash contained in a soil, that is to say, the reserve for the future. In this case it is necessary to free entirely this base from its combinations by means of hydrofluoric acid. The operation is conducted upon two grams of soil previously ignited and reduced to an impalpable powder. The decomposition is conducted in a platinum capsule by sprinkling the sample with a few cubic centimeters of hydrofluoric acid, or solution of ammonium fluorid, and adding a few drops of sulfuric acid. The mass is evaporated to dryness and dissolved in boiling hydrochloric acid. The part which remains insoluble is treated a second time by hydrofluoric and sulfuric and afterwards by hydrochloric acid. All of the potash is thus finally brought into solution. The estimation of the potash, after having obtained it in a soluble state, is conducted in the manner previously described.

Estimation of the Potash as Platinochlorid.—Instead of estimating the potash as perchlorate it can also be transformed into platinochlorid. This process gives as good results as the preceding one, but it is necessary in all cases, to separate the magnesia. After having treated the soil as indicated in the case of the estimation of the potash as perchlorate, the separation of the sulfuric and phosphoric acids, of alumina and iron, of magnesia, and the destruction of the ammoniacal salts in the manner already described, there are finally left the alkalies potash and soda in the form of carbonates. These are transformed into chlorids by adding hydrochloric acid; afterwards they are evaporated to dryness and the mixture of the two chlorids weighed in order to determine what quantity of platinum chlorid it is necessary to add, in order that it be in excess. The quantity of chlorid to be added is calculated so as to be in sufficient quantity to saturate the whole of the chlorids weighed, whether they may be composed wholly of sodium or potassium. In this way there is a certainty of having an excess of platinum. The solution of platinum chlorid used should contain in 100 cubic centimeters 17 grams of platinum. Each cubic centimeter of this solution will be sufficient for a decigram of the sodium and potassium double chlorids. After the

addition of the platinum chlorid the mixture is evaporated in a capsule with a flat bottom, on a water-bath. It is important that the temperature should not exceed 100°. If the temperature should go above this there would be a tendency to form some platinum subchlorids insoluble in alcohol.

The evaporation is continued until the contents of the dish are in a pasty condition and form a rather solid mass on cooling. It is necessary to avoid a complete desiccation. After cooling, the residue is taken up by alcohol of 95° strength. It is allowed to digest with alcohol of this strength for some time, after having been thoroughly mixed and shaken therewith in order to obtain a complete precipitation of the potassium platinochlorid. This digestion should take place under a small bell-jar resting upon a piece of ground glass. The evaporation of the alcohol is thus prevented. The mass is washed by means of alcohol of the same strength and the liquors decanted upon a small filter placed within another filter of identical weight, which serves as a tare for it on the balance. The washing is prolonged until the filtrate becomes colorless. All of the particles in the dish should be brought upon the filter by means of a hair-brush. The filters are now dried at a temperature not exceeding 95° and the platinochlorid received upon the interior filter is weighed. The precipitate may also be washed from the small filter into the capsule in which it was formed by means of a jet of alcohol. The alcohol is evaporated and the precipitate weighed in the capsule. The weighing should be made rapidly on account of the hygroscopicity of the material. The weight obtained multiplied by 0.193 gives the corresponding quantity of potash in the soil.

Purification of the Oxalic Acid.—The commercial oxalic acid used in separating the magnesia, often contains lime, magnesia, and potash. When this reagent is used in a sufficiently large quantity in the estimation of the above substances, it is indispensable to free it entirely from them. This is secured by submitting the oxalic acid to successive recrystallizations. The mother waters are thrown away. After two or three successive crystallizations the traces of potash and magnesia have disappeared and the oxalic acid obtained after ignition leaves no trace of residue.

The purification may also be secured in the following manner:

At a temperature of 60° a saturated solution of oxalic acid is made, the liquid decanted, carried to the boiling point and filtered. Five per cent of nitric acid is added and it is allowed to cool. The crystals which are deposited are collected upon a funnel in which a plug of cotton has been placed, and are washed with a little cold water.

Purity of the Ammonium Carbonate.—The ammonium carbonate employed should not leave any residue whatever on volatilization. In general, it may be said of all the reagents employed in analyses and especially of those employed in large quantities, that it is indispensable to be sure that they contain no traces of the substances which are to be estimated. The acids, ammonia, etc., should always be examined with this point in view.

Estimation of the Soda.—It is often of interest to estimate the soda in the soil, not that it is an element of any great fertility but rather because it is hurtful when in excess. It is always present in the solution prepared for the estimation of potash and is easily estimated by difference. The weight of the mixture of sodium and potassium chlorids being known when the potash is determined, the weight of its chlorids is to be deducted from the weight of the two chlorids and thus the indirect weight of the sodium chlorid is obtained.

A better way is to make a direct estimation. The soda is found entirely dissolved in the alcoholic solution obtained by washing the potash salt as before described, for the separation of the potassium platinochlorid. This alcoholic liquor is evaporated to dryness on a water-bath, in a bohemian flask of about 100 cubic centimeters capacity. The residue obtained consists of sodium platinochlorid and a little platinum chlorid. There is fitted to the bohemian flask a cork stopper carrying two tubes. The apparatus is placed upon a water-bath and kept at about 100°. Through the tube which reaches to the bottom of the bohemian flask, a current of pure hydrogen is passed. The hydrogen passes off through the second tube. The hydrogen completely reduces the salts of platinum. In order that the decomposition may go on more rapidly a few drops of water are added. When the whole mass in the flask has become black owing to the separation of the platinum, it is shaken, evaporated to dryness and hydrogen passed

through a second time. This operation is repeated three or four times, being stopped when the water no longer shows a yellow color. There is then in the flask only a mixture of reduced platinum and sodium chlorid. No trace of sodium chlorid has been lost because the temperature has never exceeded 100°. The sodium chlorid is dissolved by washing with water and filtered. The liquor, which must be absolutely colorless, is evaporated to dryness in a platinum capsule and weighed. There is thus obtained the weight of the sodium chlorid. For verification, the sum of the weight of potassium chlorid calculated from the platinochlorid and the weight of the sodium chlorid should be equal to the initial weight of the mixture of the two chlorids.

393. Potash Methods of the German Experiment Stations.[86]—*a.* To one volume of air-dried fine earth which is obtained by sifting through a three-millimeter sieve, two volumes of 25 per cent hydrochloric acid are added, or more if the soil contains much carbonate. The acid is allowed to act with frequent stirring for 48 hours at room temperature.

b. To one volume of the soil, as above prepared, are added two volumes of hydrochloric acid and the mixture allowed to stand for three hours with frequent shaking, at the temperature of boiling water.

c. (Halle method). One hundred grams of the fine earth are treated with 500 cubic centimeters of 40 per cent hydrochloric acid, made up to one liter with water and allowed to stand for 48 hours with frequent shaking. After filtering the acid extracts above described, a large aliquot part of the filtrate is evaporated for the estimation of the potash. The evaporated residue is washed into a half-liter flask in which the sulfuric acid is precipitated with barium hydroxid, the flask filled to the mark and an aliquot part of the filtrate in a half-liter flask, treated with ammonium carbonate, filtered, and the potash estimated as platinochlorid by the usual method.

394. Method of Raulin for the Estimation of Potash in Soils.[87]—The process rests upon the very feeble solubility in water of po-

[86] Die landwirtschaftlichen Versuchs-Stationen, 1891, **38** : 311.

[87] Comptes rendus, 1890, **110** : 289.

tassium phosphomolybdate, while sodium, magnesium, calcium, iron, and aluminum phosphomolybdates are more or less soluble. The process does not require complicated separation and permits of the treatment of a small quantity of soil. The weight of the phosphomolybdate obtained is equivalent to 19 times that of the potash.

The reagent is prepared by dissolving 100 grams of pure crystallized ammonium molybdate in as little water as possible and adding six and a half grams of neutral crystallized ammonium phosphate dissolved in a little water. Aqua regia is added and some ammonium phosphomolybdate is precipitated. The mixture is heated, adding a little aqua regia from time to time, until the solution of the precipitate is accomplished. The whole is then evaporated to dryness, the final temperature of evaporation not being carried above 70°. Four hundred cubic centimeters of water are added and five cubic centimeters of nitric acid, and the contents of the dish heated and filtered. The reagent is then ready for use.

The liquid to be used for washing the potassium phosphomolybdate is prepared by dissolving 20 grams of sodium nitrate in one liter of water, two cubic centimeters of pure nitric acid, and a mixture of about 20 cubic centimeters of the phosphomolybdic reagent and one and a half cubic centimeters of a solution of potassium nitrate containing 80 grams per liter, slightly heated in order to saturate the liquid with potassium phosphomolybdate. The mixture is shaken, allowed to rest, and the liquid part decanted.

For the preparation of the solution in which the potash is to be estimated, a sample of soil of such magnitude as to contain about 15 milligrams of anhydrous potash is used. The potash salts are dissolved by the usual processes and are separated from the largest part of the calcium, iron, and aluminum salts, and converted into nitrates. The solution is reduced to a volume of a few cubic centimeters and slightly acidulated with nitric acid. Four cubic centimeters of the phosphomolybdic reagent are added for every ten milligrams of anhydrous potash supposed to be present. The mixture is evaporated to dryness at 50° and immediately brought upon a very small weighed double filter, with 60 cubic centimeters

of the washing liquor mentioned above. A similar tared double filter is likewise washed with the same liquid at 50° and weighed. The weight of phosphomolybdate multiplied by 0.052 gives the anhydrous potash. This method for a direct precipitation of the potash salts does not have the merits of the perchlorate process and both are inferior in accuracy to the usual platinochlorid procedure.

395. **Russian Method for Estimating Potash in Soils.**[88]—Ten grams of the air-dried, non-ignited soil are digested with 100 cubic centimeters of ten per cent hydrochloric acid on a steam-bath for 24 hours with frequent shaking. After adding five cubic centimeters of nitric acid to the filtrate it is evaporated to dryness, taken up with dilute hydrochloric acid, filtered, the filtrate saturated with ammonia, the excess of ammonia driven off, again filtered, and the lime separated by ammonium oxalate.

The filtrate is treated with a little barium chlorid for the removal of sulfuric acid and afterwards with ammonium carbonate in excess, and left for 24 hours. After filtering, the solution is evaporated in a platinum dish, the excess of ammonia driven off, the residue taken up with water, filtered, treated with hydrochloric acid, evaporated to dryness, and ignited at low heat. The residue is dissolved in water, filtered, and the potash precipitated with platinum chlorid and estimated in the usual way.

396. **Potash Method of the Italian Stations.**[89]—The potash in the soil is determined in three forms; *viz.*,

1. Assimilable potash.
2. Potash soluble in concentrated acid.
3. Total potash.

For determination of the first, 100 grams of soil are put into a retort holding a liter and digested with dilute nitric acid.

For the analysis, an aliquot portion of the clear liquid is measured or weighed, and the determination of the potash is made by the common methods.

For an alternate method, from 20 to 50 grams of soil are put

[88] Thoms, Zur Wertschätzung der Ackerde, Second Contribution Riga, 1893, 120.

[89] Le Staioni Sperimentali Agrarie Italiane, **16** : 679.

into a retort of 500 cubic centimeters, moistened with water, and nitric acid is gradually added. After one or two hours there are added from 200 to 300 cubic centimeters of water; the liquid is poured without filtering into a retort and the residue washed by decantation.

In the liquid, after the elimination of the other substances with barium chlorid, ammonium carbonate, etc., the potash is determined by the ordinary methods.

In the second case, by using warm concentrated acids, a portion of the insoluble silica is decomposed, but this decomposition is always partial and the quantity of the potash extracted depends upon the temperature, upon the concentration, upon the duration of the action, and upon the nature of the acid.

The method of moistening from 20 to 50 grams of the soil with water and adding concentrated nitric acid of 1.20 density, in such a manner that the soil shall be completely saturated, may also be employed. Then the temperature is kept at 100° during two hours. In the solution, the potash is determined as usual.

In the third case the soil is decomposed by hydrofluoric and sulfuric acids, or by fusion with alkaline carbonates, and the total potash determined by one of the standard methods.

If it is desired to adopt a general method for the determination of the potash the following points must be carefully considered:

1. The quantity of the soil to be examined.
2. The state of humidity or dryness of the same.
3. The quantity, nature, and concentration of the acid.
4. The quantity of the water.
5. The duration of the treatment.

397. **Method of J. Lawrence Smith for Potash.**—This method, designed especially for mineral analysis, has been fully approved by the general experience of analysts.

The principle of the method[90] depends upon the decomposition of silicates on ignition with calcium carbonate and ammonium chlorid. The object of this mixture is to bring into contact with the mineral, caustic lime and chlorid of lime in a nascent state at a red heat, the caustic lime being soluble to some extent in calcium

[90] Crookes, Select Methods in Chemical Analysis, 3rd edition, 1894 : 26.

chlorid at a high temperature. Pure calcium carbonate, made by precipitation of marble, should be used.

The ammonium chlorid should be prepared from crystals of pure, sublimed sal ammoniac, by dissolving in water, and filtering and evaporating the solution until small crystals are deposited, the solution being well-stirred until one-half or two-thirds of the whole has crystallized. The mother-liquor is poured off while still hot, and the crystals dried on an asbestos filter at ordinary room temperature.

A special platinum crucible should be used in the Smith method, but the common crucible, especially if very deep, can be employed. The special crucible is of about double the usual length. Smith recommends a crucible 95 millimeters in length, diameter at top 22 millimeters, at bottom 16 millimeters, and weighing from 35 to 40 grams. The object of the long crucible is to have the part of the bottom containing the silicate subjected to a high heat, while the top of the crucible is at a much lower temperature, thus preventing the loss of alkalies by volatilization.

Method of Analysis.—The samples of soil or silicate containing the alkalies are well pulverized in an agate mortar, and from one-half to one gram of the finely pulverized material used for analysis. This is carefully mixed with the same weight of finely powdered sal ammoniac and the mineral and sal ammoniac rubbed well together in a mortar. Eight parts by weight of calcium carbonate are added in three or four portions, and the whole intimately mixed after each addition. The contents of the mortar are emptied on a piece of glazed paper and then introduced into the crucible, which is tapped gently upon the table until the contents are well settled. It is fixed in the furnace which is used for heating, and a small Bunsen burner is placed beneath the crucible, and the heat applied just about at the top of the mixture and gradually carried toward the lower part until the sal ammoniac is completely decomposed, which requires from four to five minutes. A greater heat is then applied by means of a blast-lamp and the crucible kept at a bright redness for from 40 to 60 minutes. The crucible is allowed to cool, the contents detached and placed in a platinum or porcelain dish of about 150 cubic centimeters capacity, and from 60 to 80 cubic centimeters of distilled water

added. The solution of the flux may be hastened by heating the water to the boiling point. The crucible and its cover are also well washed with hot water until all matter adhering to them is dissolved. After the slaking of the mass it is best to continue the digestion with hot water for six or eight hours, although this is not absolutely necessary. The contents of the crucible are filtered and washed well with about 200 cubic centimeters of water. The filtrate contains in solution all the alkalies of the mineral, or soil, together with calcium chlorid and caustic lime. A solution of pure ammonium carbonate containing about one and one-half grams of the pure salt is added to the filtrate. This precipitates the lime as carbonate. This dish containing the material is placed on a water-bath and its contents evaporated to about 40 cubic centimeters. Two additional drops of ammonium carbonate are added, and a few drops of caustic ammonia, to precipitate any lime which may be redissolved by the action of the ammonium chlorid solution on the calcium carbonate. The contents of the dish are brought onto a small filter and washed with as little water as possible and the filtrate received in a small beaker. The filtrate contains all the alkalies as chlorids, together with a little ammonium chlorid. A drop of ammonium carbonate solution is added to ensure the precipitation of all the lime. If no more lime be present evaporate on a water-bath in a deep platinum dish, in which the alkalies are to be weighed. The dish should have from 30 to 60 cubic centimeters capacity, and during the evaporation should never be more than two-thirds filled. After the evaporation has been completed the dish is slowly heated and then gently ignited over a gas-flame to drive off any ammonium chlorid which may be present. During this process the platinum dish may be covered with a thin piece of platinum to prevent any possible loss by the spitting of the salt after the ammonium chlorid has been driven off. The heat should be gradually increased until it is brought to a point a little below redness, leaving the cover off. The platinum dish is again covered, and when sufficiently cooled placed on a balance and weighed.

If lithium chlorid be present it is necessary to weigh it quickly as the salt being very deliquescent takes up moisture rapidly. The alkalies may now be separated in the usual way.

If the sample under examination contains magnesia the residue in the capsule should be dissolved in a little water and sufficient pure lime-water added to render the solution alkaline. It should then be boiled and filtered. The magnesia will, in this way, be completely separated from the alkalies. The solution which has passed through the filter is treated with ammonium carbonate in the manner first described, and the process continued and completed as above mentioned.

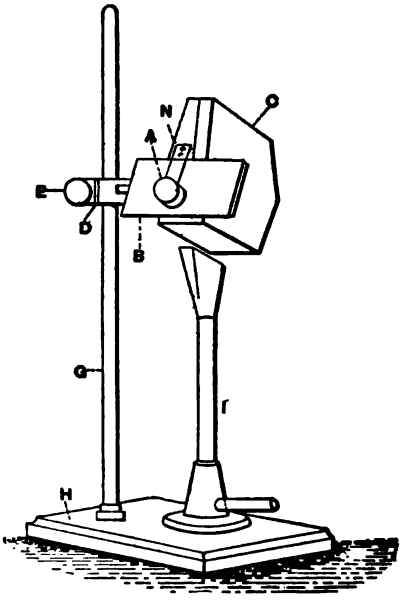

Fig. 81. Smith's Muffle for Decomposition of Silicates.

If it be suspected that the whole of the alkalies have not been obtained by the first fusion, the residue upon the filter can be rubbed up in a mortar with an amount of ammonium chlorid equal to one-half the weight of the mineral, mixed with fresh portions of calcium carbonate and treated exactly as in the first instance. Any trace of alkali remaining from the first fusion is thus recovered in the second one.

Method of Heating the Crucible.—The apparatus used by Smith for igniting the crucible is shown in Fig. 81. It consists

of an iron filter-stand HG, a clamp, ED, carrying the muffle NC, attached by the supports AB, and heated by the lamp F. The muffle NC is a chimney of sheet iron, from eight to nine centimeters long, ten centimeters high, the width at the bottom being about four centimeters on one side and three centimeters on the other. It is made with the sides straight for about four centimeters and then inclined toward the top so as to leave the opening at the top about one centimeter in width. A piece is cut out of the front of the chimney of the width of the diameter of the hole in the iron support and about four centimeters in length, being semi-circular at the top, fitting over the platinum crucible. Just above this part of the chimney is riveted a piece of sheet iron in the form of a flattened hook, N, which holds the chimney in place by being slipped over the top of the crucible support; it serves as a protection to the crucible against the cooling effects of the currents of air.

398. International Method for Assimilable and Total Potash.— In the International Congress of Chemists held in Paris in 1889,[91] the discrimination between the assimilable and total potash was declared to be of prime importance. Unfortunately no method is known by which the potash which is present in the soil in a state suited to the wants of plants can be determined with entire accuracy. In general, that portion which is given up to weak acids may be assumed to be available. In the treatment of soils with weak acid, as pointed out in the Congress, it is demonstrable that with a 0.05 to 0.1 per cent nitric acid solution, the quantity of potash which goes into solution increases by continued stirring of the mixture with the time of action of the acid up to a certain maximum which is reached in from three to four hours, and after that, it is not changed even when the strength of the acid mixture is increased to two per cent. From this time on, concentrated acids withdraw from the soil which has already been exhausted by the weak acid, a new quantity of potash. The soils which have been exhausted by concentrated acids yield also an additional quantity of potash when they are treated with hydrofluoric acid, or melted with baryta or sodium carbonate. Potash, therefore, appears to exist in the soil in various forms.

[91] Chemiker Zeitung, 1889, **13** : 1391.

First. In the form of undecomposable silicates which have, agriculturally perhaps, very little interest.

Second. In the form of silicates which are more basic than those just mentioned. These silicates are attacked by strong acids and give up probably every year a portion of their potash to vegetation.

Third. In a form which is easily soluble in weak acids and consequently directly assimilable by plants.

In view of the fact that it would be of interest to chemists and agronomists to establish certain methods of investigation so as to be able to obtain comparative results, it was decided to adopt the original method recommended by Gasparin for the estimation of the potash decomposable by concentrated acids. This method consists in the treatment of the soil with boiling aqua regia until the sand which is not decomposed, is white.

Determination of the Fineness of the Earth which is Used for Analysis.—For the estimation of potash, the soil should be divided as finely as possible, and passed through a sieve of 30 meshes to the centimeter. The decomposition is then completed in two hours, while if a sieve of only ten perforations per centimeter is used, the acid must be allowed to work for 12 hours.

The determination of the potash after solution, is accomplished by any of the standard methods.

399. **Method of Tatlock as Used by Dyer.**—Attention was called in paragraph 367 to the estimation of the total plant food in the soil by extraction of the sample with citric acid. Dyer first determines the total potash by Tatlock's method which is as follows:

To determine potash, ten grams of fine dry soil are treated with ten cubic centimeters of hydrochloric acid and evaporated to dryness on the water-bath, the residue taken up with another ten cubic centimeters of acid, warmed, diluted with water, boiled, filtered, and washed. The filtrate and washings are concentrated and gently incinerated to get rid of organic matter, and the residue redissolved in hydrochloric acid, and evaporated slowly with a considerable quantity of platinum chlorid. If the evaporation be conducted slowly, the potassium platinochlorid settles out well, despite the iron, aluminum, and calcium salts, and is easily washed with some more platinum chlorid solution, followed by alcohol.

The application of this modification of the platinum chlorid process to solutions containing comparatively minute quantities of potash in a great excess of iron, aluminum, and calcium salts is probably new to many chemists. It works admirably, and obviates the necessity for removing iron, aluminum, calcium, magnesium, etc., with the necessary use of ammonia, and the tedious processes of concentration and final volatilization of the ammonium salts; but, of course, the process cannot be employed if soda also is to be determined.

The potash, soluble in hydrochloric acid, having been thus determined, the undissolved siliceous matter is incinerated, weighed, and finely ground in an agate mortar. A weighed portion of it is then, as in the Smith method, mixed with a large bulk of pure calcium carbonate and a little ammonium chlorid and heated, beginning with a low temperature, rising slowly to bright redness. The mass is then boiled with water, washed, incinerated, reground, mixed with some more ammonium chlorid, and again heated, boiled, and washed. The process is repeated and the filtrates from all the treatments concentrated, the calcium being removed as carbonate, and the potash determined in the filtrate, after evaporation and incineration at a low temperature, by means of platinum chlorid.

When it is desired to extract the soluble matters with a dilute organic acid 500 cubic centimeters of the citric acid solution of the soil, made as described in paragraph 367, corresponding to 50 grams of soil, are evaporated to dryness in a platinum dish and ignited at a low temperature. The residue is dissolved in hydrochloric acid, filtered, and washed, and the filtrate again evaporated to dryness and treated again as just described. The potash is then determined as above.

400. Moore's Method of Estimating Potash.—In the various methods of determining potash which have been described, except that of Tatlock, it is seen that preliminary to the final process the various bodies with which the potash is associated, such as lime, alumina, iron, titanium, phosphoric acid, etc., must first be removed. The principle underlying Tatlock's and Moore's methods is based on the possibility of securing the content of potash without this troublesome separation. The conduct of the Moore method is as follows:[92]

[92] Journal of the American Chemical Society, 1898, **20** : 342.

The material under examination is brought into solution in acid, ammonium salts, and organic matter destroyed with aqua regia and the excess of acid removed by several evaporations to dryness, care being taken to break up all nitrates with hydrochloric acid. The residue is taken up with water and a few drops of hydrochloric acid, filtered and washed thoroughly. To the filtrate a slight excess of chlorplatinic acid solution is added and evaporated on the steam-bath nearly to dryness so that the salts solidify on cooling. It is important that the evaporation be not carried to complete dryness as the dry iron and aluminum chlorids are exceedingly difficult to dissolve in acidified alcohol. To the cooled mass add from 15 to 25 cubic centimeters of acidified 90 per cent alcohol, stir, and let stand several minutes, filter, wash with alcohol and ammonium chlorid solution and dry in the usual manner. Dissolve the potassium chlorplatinate in hot water, evaporate, dry in water oven for one-half hour, and weigh. The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool 90 per cent alcohol until one cubic centimeter of the alcohol neutralizes about 2.3 cubic centimeters of normal alkali.

This method permits both potash and phosphoric acid to be estimated in a very small sample of material and has been tried over several years in the Bureau of Chemistry by many different analysts, both on soils and plants with the happiest results.

It has lately again been subjected to a critical examination by Veitch,[93] who applied it in comparison with the official method to 35 samples of soil with the following results:

TABLE I.—POTASH IN SOILS.

	Filtered on paper. Acid alcohol.			Filtered on gooch crucible. Acid alcohol.	
	Official method. Per cent.	Moore method. Per cent.		Official method. Per cent.	Moore method. Per cent.
2134	0.39	0.42	2153	0.12	0.13
2135	0.27	0.27	2154	0.10	0.12
2136	0.18	0.18	2155	0.93	0.84
2137	0.52	0.65	2156	0.60	0 63
2138	0.41	0.40	2157	0.85	0.85
2139	0.23	0.24	2158	1.06	1.07
2140	0.14	0 12	2159	0.15	0.16
2141	0.27	0.34	2160	0.18	0.21
2142	0 29	0.27	2161	0.43	0.47
2143	0.29	0.27	....	....	....
Average	0.299	0.305	....	0.496	0.497

[93] Journal of the American Chemical Society, 1905, **27** : 56.

	Plain alcohol.			Plain alcohol.	
2144	0.44	0.42	2162	0.48	0.48
2145	0.48	0.50	2165	0.08	0.09
2146	0.47	0.47	2166	0.38	0.41
2147	0.50	0.48	2168	0.44	0.48
2149	0.44	0.42	2169	0.21	0.21
2150	0.60	0.62	2170	0.21	0.22
2151	0.78	0.82	2171	0.11	0.12
2152	0.67	0.66	2172	0.10	0.11
Average	0.547	0.548	....	0.25	0.265
General average	0.41	0.41	....	0.38	0.39

The results are given just as they were obtained in the regular routine of the laboratory; they were not repeated nor were any rejected. In some cases the differences are larger than they should be between duplicates, but as the average results are practically identical it seems fair to consider such differences as due to the analytical work rather than to the method itself.

The results are not noticeably different where the filtration and washing were done on paper rather than on the gooch, and under some conditions the use of paper presents centain advantages as the potassium chlorplatinate may be dissolved in order to separate it from foreign salts, and the solution evaporated, dried and weighed in platinum dishes. The combined iron and aluminum oxids ranged from five to 25 per cent in these samples. No particular advantage appears to result from the use of the acidified alcohol as recommended by Moore, at least where the amount of lime salts, more especially calcium sulfate, is not large. It would appear, therefore, that the method may be further simplified by substituting ordinary 90 per cent alcohol for the acidified alcohol.

This method has many advantages over any other in use where only potash and phosphoric acid are to be determined.

401. Estimation of Total Alkalies and Alkaline Earths.—To properly determine the exact amount of these substances in a sample of soil it is necessary first to remove the silica. This is accomplished in the process of Berthelot and André[94] by intimately incorporating with the sample, in a state of very fine powder, four or five times its weight of ammonium fluorid, in a platinum

[94] Annales de Chimie et de Physique, 1888, [6], **15** : 89.

dish, and heating gently without passing a pasty state. After cooling the mixture, it is moistened with strong sulfuric acid and gently heated until all acid fumes have disappeared, but the mass is not raised to a red heat. If there is any doubt about the complete decomposition of the silica the treatment is repeated.

The results of treating soils with other solvents to ascertain the quantities of potash and other substances dissolved are also given in the article cited. The solvents used are water, sweetened water, acetic ether, acetamid, ammonia, carbonic acid, acetic acid, dilute hydrochloric acid, dilute nitric acid, dilute hydrochloric acid in motion, cold and hot, concentrated hydrochloric acid in motion, cold and hot, and pure nitric acid, cold and hot.

Comparison of Fluorin Method with Common Methods.—To establish the difference in the data obtained by the old and new processes samples of the same earth were treated by Berthelot and André by different methods with the following results:

	By the fluorin method. Per cent.	By the cold dilute hydrochloric acid method. Per cent.	By the concentrated hydrochloric acid method. Per cent.	By incineration and subsequent treatment with boiling hydrochloric acid method. Per cent.
Potash	0.886	0.021	0.149	0.176
Soda	0.211	0.024	0.033	0.042
Magnesia	0.087	0.033	0.033	0.067
Lime	1.160	0.879	1.120	1.060
Alumina	3.950	0.102	1.009	2.631
Ferric oxid	2.150	0.296	1.401	1.678

The impossibility of getting all the alkalies and oxids into solution by even the prolonged action of a boiling acid is clearly set forth in the above table. Boiling sulfuric acid might do a little better but would not give correct results. Lime alone of the elements in the soil can be correctely determined by solution in boiling hydrochloric acid, a circumstance due to the fact that lime is found chiefly as carbonate, sulfate, and phosphate in the soil, and these compounds are easily soluble in hot hydrochloric acid with the exception of the sulfate. Even lime could not be thus determined in soils containing silicates rich in lime. The other mineral elements cannot be entirely dissolved by the common methods. This is due to the forms in which they occur, being

mostly silicates of different composition, usually with excess of silica.

As to the silicates they may be divided into two groups. The first of these are the hydrated silicates, resembling the zeolites, capable of being completely decomposed by boiling acids. The first group of silicates is doubtless of greater importance to vegetable life than the second since it would, doubtless, give up its alkalies with greater ease. This distinction is, however, arbitrary. It is, in fact, impossible to place on one side the soluble and on the other, the insoluble silicates. This distinction represents only the unequal degrees in the speed of decomposition of the different silicates contained in the primitive rocks under the influence of atmospheric agents, the soil being nothing more than the products of the decomposition of these rocks with vegetable mold. The second group is insoluble in acids.

That part of the silicates least decomposed at any given moment will be attacked more easily by acids, while that portion whose decomposition has been pushed furthest will be more slowly attacked. The action of the acid will grow more feeble as the time of contact is prolonged, and after a time a point is apparently reached where the results are nearly constant. But it is evident that this distinction is purely conventional and bears no necessary or even probable connection with the quantity of alkali really assimilable by plants.

Vegetables, moreover, exert on a soil, for the extraction of its alkalies and other matters, chemical reactions peculiar to themselves, altogether distinct from the tardy action of atmospheric agents and still more distinct from the rapid action of mineral acids.

It is well known with what energy, it ought to be said with what admirable instinct, plants take from the soil the least traces of phosphorus, of sulfur, of potash, of iron, and other substances necessary to their sustenance.

These specific actions of vegetables on the soil merit, in the highest degree, the attention of analysts and agronomists. Their intervention plays a most important part in the restitution to the soil, by means of complementary fertilizers, the mineral elements removed by vegetable growth.

402. Estimation of Lime by the French Method.—The quantity of lime contained in the soil varies within wide limits. Sometimes this base is entirely absent to such a degree that it is even impossible to discover feeble traces of it. Sometimes it composes almost the whole of the earthy mass. Lime is found in the soil, principally in the state of carbonate. It is also found combined with organic matter under the form of humates, with sulfuric acid, silicic acid, etc. It is customary to estimate the lime as a whole, without distinguishing between the different states in which it exists. The quantity of material which is used in the method[95] prescribed by the sub-committee on methods of analysis of the consulting committee of the agricultural stations and laboratories of France varies in proportion to the amount of calcareous matter contained in it. For a soil which contains a large amount of lime, one or two grams is sufficient for the analysis. For a soil which is poor in calcareous matter ten or even 20 grams are necessary. The quantity of lime dissolved in a given soil differs according to the kind and strength of the acids employed and length of contact of the acid with the soil. The calcium carbonate, the sulfate, the nitrate, and the humate rapidly pass into solution when treated with acids as above, but this is not the case with calcium silicates which are attacked much more slowly. Sometimes the silicates give only an insignificant increase in the amount of lime, and in this case it is immaterial what process of solution is employed. For simplicity it is best to adopt the method of solution in boiling concentrated nitric acid, prolonging the boiling for a period of five hours. This method of operation is sufficient to bring into solution at one treatment, not only the lime, but also the potash and magnesia. After having heated with acid for the necessary time there are added in the capsule in which the solution takes place ten cubic centimeters of nitric acid and 50 cubic centimeters of water. The mixture is heated, collected upon a filter and the residue washed. To the filtrate, the volume of which should be from 400 to 500 cubic centimeters, a sufficient quantity of ammonia is added to render it slightly alkaline. There is formed a precipitate of alumina and of iron oxid containing phosphoric acid and also sometimes a trace of the lime combined with the same acid.

[95] Annales de la Science Agronomique, 1892, 8th year, 1 : 270 et seq.

In order to keep the whole of the lime in solution it is necessary to add a little acetic acid, about ten cubic centimeters more than is necessary to neutralize the ammonia which has been added. If the liquid is turbid on account of the presence of the iron and aluminum phosphates it is necessary to filter it. There is afterwards added a slight excess of ammonium oxalate in solution, and the whole is left for 24 hours in order that the calcium oxalate may deposit. The complete precipitation is not always immediate, and especially in the presence of magnesia it takes place with slowness. The calcium oxalate is collected upon a filter and washed with hot water. To determine the quantity of the lime the best procedure consists in transforming the oxalate into carbonate by a careful ignition, and afterwards heating to a high temperature for some time. The oxalate for this purpose should be contained in a covered platinum crucible. By this method the calcium carbonate is transformed into calcium oxid, in which form it is weighed rapidly to avoid absorption of moisture.

Instead of proceeding as above, the lime may be weighed as sulfate. For this purpose the calcium oxalate is transformed into carbonate by ignition in a platinum crucible. Afterwards it is treated with nitric acid until the carbon dioxid is completely driven off. The platinum crucible is covered with a funnel which is afterwards washed in order to bring back into the dish the small drops which have been projected in the process of boiling. An excess of sulfuric acid is added and evaporated to dryness on a sand-bath. Afterwards, in a muffle, the temperature is carried to a feeble redness until the vapors of sulfuric acid are all driven off. The lime is weighed in the form of sulfate, and the weight multiplied by 0.412 gives the lime contained in the quantity of soil used.

In special researches in which it is desired to avoid attacking the siliceous pebbles of the soil, the concentrated nitric acid is replaced by dilute nitric acid in slight excess, and heated for a few moments only. The calcium carbonate is then dissolved with the other calcareous salts not combined with silica in the rock products. The analysis is continued in other respects as just described.

403. Estimation of the Actual Calcium Carbonate.—The lime which is found in the state of carbonate plays one of the most important rôles in the chemical phenomena which take place in the soil. It is often of great importance to determine it. The most certain process is to estimate the carbon dioxid which is disengaged from the carbonate under the influence of an acid and to receive this gas in a jar graduated to measure it by volume. The flask recommended by the French Committee for this purpose contains about 300 cubic centimeters. The neck of the flask is connected with a condensing tube of about one centimeter interior diameter, which is cooled by a current of water.

According to the presumed richness in calcium carbonate varying quantities of soil are employed for analysis, from as little as half a gram for soils which are rich in carbonate, up to five or even ten grams for soils which are poor in carbonate. The apparatus is connected with a mercury pump for the purpose of exhausting the air as completely as possible therefrom. For this purpose the flask in which the carbonate is disengaged is made in the shape of a tubulated retort. Through the opening into the retort, a narrow tube is introduced and connected with a small funnel by means of a rubber tube supplied with a pinch-cock. When the retort has been connected with the mercury pump a slight vacuum is produced and the pinch-cock is opened and 40 cubic centimeters of distilled water allowed to enter. The pinch-cock is closed soon enough to retain a portion of the water in the funnel. The retort is then heated and a vacuum partially produced by means of the pump. When the flask is boiling, the steam drives out the air. A refrigerating jacket is connected with the tube leading from the retort to the pump by means of which the steam is condensed and falls back into the flask. After some minutes of boiling, a vacuum is produced; the lamp is then taken away and a cylinder, graduated at 100 cubic centimeters and filled with mercury, is placed over the lower orifice of the pump, and there is introduced into the apparatus, by the funnel above described, some hydrochloric acid in small quantities, but sufficient only to saturate the whole of the carbonate in the sample of soil. Usually three or four cubic centimeters will be sufficient. The acid should be added in such quantities as to pre-

vent the production of any large amount of foam. If frothing should be excessive a little oil can be added to the flask. The whole of the carbon dioxid produced in the reaction is withdrawn by means of the mercury pump and collected in the graduated jar. Towards the end of the operation the flask is heated anew in order to produce an ebullition which is continued for some time. The volume of gas collected is measured after making the proper corrections for pressure and temperature. Afterwards the carbon dioxid which has been produced is absorbed by two or three cubic centimeters of a solution of potash of 42° Baumé. This potash is introduced into the graduated jar by means of a pipette bent into the form of a U in the lower portion. If the whole of the gas is not absorbed the volume which remains is read, and this is subtracted from the original volume after having made the proper corrections for pressure and temperature. The difference gives the quantity of carbon dioxid contained in the amount of earth employed. From this the actual weight of the calcium carbonate is complete. This official French method does not appear to possess any advantage in accuracy to the usual absorption method and is far more complicated.

404. Estimation of the Active Calcareous Matter in Soils.—Like other soil elements, the calcium carbonate exists in different degrees of fineness and availability in the soil. It must be admitted that the fine particles play the most important rôle. The calcium carbonate, which exists in large fragments, presents only a circumscribed surface and remains almost inactive, although it is easily corroded by the rootlets of plants. It is possible to estimate in a rapid way, the quantity of fine carbonate in the soil, considering that in a time relatively short, feeble acids act upon calcareous matter proportionally to the surface which it presents, and that it attacks, therefore, especially the finest particles. By measuring the amount of carbon dioxid set free under the action of dilute acids it is possible to estimate the content of available calcareous matter in the soil.

The apparatus of Mondesir is recommended for this purpose by the French Committee. It is composed of a tubulated flask of about 600 cubic centimeters capacity. The interior tubulature carries a manometer fixed by means of a stopper. This is formed

of a rubber tube, terminated by a glass tube, whose extremity is united to a little rubber bag, very flexible, placed in the interior of the flask.

Graduation of the Apparatus.—If the apparatus is new it is necessary to begin by graduating it. The rubber bag is filled with water, the air being carefully excluded, in such a way that the level of the water comes just a little above the bend in the tube. There are placed in the flask 125 cubic centimeters of water and it is shaken for a few seconds. The flask and the manometer are then unstoppered and the level of the water in the manometer is made to equal the level of the water in the flask. With a rubber ring the level of the water in the manometer tube is marked. The manometer is then stoppered. There is added to the flask two-tenths gram of pure calcium carbonate. The flask is closed and shaken for a minute. There is then added, enclosed in a little piece of filter paper, six-tenths of a gram of pulverized tartaric acid and the flask immediately closed and shaken several times. The manometer tube is then uncorked and moved until the level of the water reaches the point marked before. The difference in level after the height of the water remains constant is then read. The depression in the level observed, corresponds to carbon dioxid from two-tenths gram of pure calcium carbonate.

405. Estimation of the Available Calcareous Matter in the Soil. There is introduced into the flask of the apparatus a quantity of soil varying in amount in accordance with the content of carbonate which it is supposed to contain. There are added 125 cubic centimeters of water and the flask is shaken for a minute. As in the test given before, the level of the water in the manometer is then made to correspond to that of the water in the flask. The level in the manometer is marked as before with a rubber band, and the manometer is closed. There are then added, contained in a piece of filter paper, two grams of pulverized tartaric acid and the operation is finished as described before. The amount of tartaric acid added, in general, should be three times as much as the amount of calcium carbonate supposed to be contained in the earth. The pressure in the manometer being proportional to the quantity of carbon dioxid disengaged, it is easy to calculate the

quantity of calcium carbonate in a state of fine division contained in the soil taken for the test.

In order to fill the rubber bag it is necessary to put it in its proper place in the apparatus. The flask is filled with water in order to flatten the rubber bag and expel the air from it. It is then closed with a cork. Afterwards, with the aid of a small funnel and with a copper wire placed in the tube, the lower extremity of which descends just to the elbow, the air in the tube is replaced by water. The operation is finished by uncorking the flask and inclining it or shaking it after a partial vacuum has been established. It is useless to attempt to drive off the last particles of the air. The rubber bag should have a content of about double the volume of the whole of the interior of the manometric tube. In the washing which is necessary between two successive operations, it is well to fill the flask entirely with water in order to expel all the carbon dioxid which it may contain.

The same remark may be made of this method of determination as was made of the last one. In the present case, however, the operation is not quite so complicated. When the apparatus is once arranged, it will admit of rapid determinations.

406. Lime Method at the Swedish Station.—A method of estimating lime in soils which is somewhat different in principle from those usually followed is employed in Sweden.[96]

The lime solution is prepared by digesting 150 grams of fine soil with 500 cubic centimeters of a ten per cent hydrochloric acid solution for 48 hours with frequent shaking. The free carbonates which may be present are first neutralized with acid before beginning the operation above noted. The solution is poured on a dry filter and the lime determined in the filtrate in the following manner: Fifty cubic centimeters corresponding to 15 grams of soil are boiled in a 100 cubic centimeter flask with a little potassium chlorate, nearly neutralized with ammonia and boiled with sodium acetate with the purpose of precipitating the greater part of the iron silica and phosphoric acid. The mass is cooled rapidly, the volume made up with water to 100 cubic centimeters, poured on a dry filter and 50 cubic centimeters of the filtrate correspond-

[96] Experiment Station Record, 1894-95, **6** : 22.

ing to 7.5 grams of soil treated with an excess of acetic acid, and the lime precipitated hot by ammonium oxalate.

The precipitate is washed, dried and ignited for ten minutes over the blast-lamp, dissolved in an excess of standard hydrochloric acid solution, the excess of acid determined by titration, and the quantity of calcium oxid dissolved by the acid computed.

The principle on which this method is based is seen to be the precipitation and conseqeunt separation of the lime in an acetic acid solution as oxalate, the conversion of the oxalate into oxid, and the determinations of the oxid from the quantity of acid required to convert it into chlorid.

407. Estimation of Assimilable Lime.—In the determination of the total lime in soils or even of that part present as carbonate, it is not to be assumed that the quantity assimilable by plants is known; particles of lime minerals in soils are corroded only superficially by the rootlets of plants and any process which would attack only the superficies of the lime particles would thus more nearly resemble the activity of the solvent forces of plant growth. Oxalic acid is a reagent of this kind, attacking only the surfaces of lime particles. Reverdin and de la Harpe guided by this fact have based a method for determining the amount of lime present in the soil in an available state on the solvent action of oxalic acid.[97] After the total lime content has been determined, 20 grams of the soil sample are covered with 200 cubic centimeters of a solution containing in molecular proportion a known quantity of sodium oxalate and carbonate. The mixture is digested on the water-bath for one hour. By this treatment all lime minerals are converted superficially into oxalate while particles containing magnesia are not affected. After filtering and washing well, the filtrate and wash-waters are acidulated with hydrochloric acid. If any precipitate of organic matter be produced it is separated by filtration. The filtrate is treated with a slight excess of sodium acetate by which process the excess of hydrochloric acid is replaced with acetic acid after which the oxalic acid may be separated by treatment with calcium chlorid and subsequently titrated with potassium permanganate in presence of excess of sulfuric acid. The oxalic acid obtained, deducted from

[97] Chemiker Zeitung, 1889, **13** : 726.

the quantity originally present will give the amount consumed on the surfaces of the lime particles and consequently the amount of lime corresponding thereto which may be considered as available for plant growth.

408. Method of the Halle Station for Lime.[98]—a. *In Phosphates, Limestones, Etc.*—Four grams of the prepared sample are heated with 50 cubic centimeters of hydrochloric acid and five cubic centimeters of nitric acid, in a porcelain dish on the water-bath to dryness, and left for a few hours at 105° for the purpose of separating the silicic acid. The dry residue is moistened with hot water and a few drops of hydrochloric acid, and allowed to stand for some time with frequent stirring. The contents of the dish are then washed into a half-liter flask, which is filled up to the mark and the separated silica removed by filtration. If the silicic acid is not taken into account, the solution can be made directly in a half-liter flask.

After filtration, an aliquot part of the filtrate is neutralized in a 250 or 500 cubic centimeter flask with ammonia, again acidified with a few drops of hydrochloric acid and allowed to stand six hours at least, in the cold, with ammonium acetate. For each four grams of the substance 50 cubic centimeters of an ammonium acetate solution are used, made by dissolving in one liter of water 100 grams of ammonium acetate. If phosphoric acid is present in excess, iron and aluminum oxids are precipitated completely as phosphates. If iron and aluminum oxids are in excess, the excess must be precipitated by ammonia. If it is feared that in the subsequent precipitation of the lime by ammonium oxalate there may be still some phosphoric acid in solution, before precipitation with ammonium acetate the proper amount of ferric chlorid is added and the iron is afterwards precipitated with ammonia. It is certain that in the presence of oxalic acid and phosphoric acid the lime is precipitated as oxalate, but should it be feared that traces of calcium phosphate are precipitated with the iron and aluminum phosphates the precipitate of iron and aluminum phosphates may be dissolved in hydrochloric acid, neutral-

[98] Bieler and Schneidewind, Die agrikultur-chemische Versuchsstation, Halle a/S, Berlin, 1892 : 80.

ized with ammonia, again acidified and a second time precipitated with ammonium acetate and the filtrate added to that first obtained.

For the further estimation the filtrates are united and a quantity corresponding to a given part of the original sample, and being in volume from 50 to 100 cubic centimeters is made slightly acid with acetic acid and while hot precipitated with dilute ammonium oxalate. The filtrate must contain acetic acid since calcium oxalate is best precipitated from a slightly acetic acid solution. The filtering of the calcium oxalate should not take place until from six to 12 hours after precipitation, and during this time it should stand in a warm place. Filter paper of the best quality should be used for the purpose.

The dried precipitate is brought into a platinum crucible together with the filter; the filter is first incinerated over an ordinary Bunsen and the calcium oxalate converted into calcium oxid by ignition for 15 minutes over the blast. It is then cooled in a well-closed desiccator and weighed as oxid. If in the precipitation of the iron and aluminum phosphates sodium acetate be employed instead of ammonium acetate, the precipitation must take place hot and filtration also be accomplished on a hot filter.

b. *Estimation of Lime in Soils.*—For the estimation of lime in soils there may be used either the acid soil-extract, prepared as under the direction for the estimation of potash, or 20 grams of the soil may be treated with hydrochloric acid and a few drops of nitric acid, and evaporated to dryness in a porcelain dish and the silicic acid separated as described for the estimation of lime in phosphates and limestones. In the case of soils, iron and aluminum oxids can be precipitated directly with ammonia since the small quantity of phosphoric acid usually contained in soils is not sufficient to influence in any way the estimation of the lime. For example, suppose there is 0.10 per cent of phosphoric acid contained in a soil. In case the whole of this phosphoric acid is taken down with the lime it would only amount to about 0.10 per cent of calcium oxid precipitated as phosphate. This case, however, is very improbable since it is much more likely that the iron and aluminum phosphates will be precipitated and the whole of

the phosphoric acid be carried down with them instead of being precipitated with the lime.

The precipitation of the lime and its subsequent treatment are to be conducted as just described.

409. Estimation of Magnesia.—Magnesia usually is found in much smaller quantities than lime in the soil. It is necessary to operate upon considerable quantities of the sample in order to determine the magnesia with precision and especially when it occurs in minute proportions. The procedure recommended by the French Committee is as follows:[99] From ten to 20 grams of the soil are used. The decomposition is accomplished as in the case of the lime determination. A few drops of barium nitrate are added for the purpose of precipitating any sulfuric acid present. Some ammonia and ammonium carbonate are added to precipitate the iron and aluminum oxids, the lime and the excess of barium introduced, as well as the phosphoric acid. The operation is best conducted on a dilute solution having a volume of from 400 to 500 cubic centimeters. The solution from which the lime has been precipitated, contains with the magnesia, large quantities of ammoniacal salts which it is necessary to destroy. For this purpose the solution is concentrated in a flask until its volume is about ten cubic centimeters. About ten cubic centimeters of nitric acid are added and the whole brought to the boiling point, and a few drops of hydrochloric acid added. Continuing the heating, hydrochloric acid is added in small portions and, from time to time, some nitric acid until the bubbles indicating the setting free of gaseous nitrogen, resulting from the action of the nascent chlorin upon the ammonia, have completely ceased to appear. The whole is then evaporated on a sand-bath in a porcelain dish in order to separate the silica. The residue is taken up by water containing a few drops of nitric acid. The filtrate is evaporated to dryness in a covered porcelain dish. Upon the residue four or five grams of oxalic acid, in a state of powder, are placed and a little water is added in such a way that the moist mass covers the matter in the dish. In order to avoid all losses there is placed upon the dish a funnel which serves as a cover. The dish is heat-

[99] Annales de la Science agronomique, 1891, 8th Year, 1 : 275.

ed on a sand-bath, and when the film which is formed begins to break there are added from time to time, a little more oxalic acid and water until there is no longer any disengagement of the vapor of nitric acid. Afterwards evaporation is carried to dryness and the heat raised to a low redness. The magnesia is found in a free state or mixed with alkalies. It is washed with a small quantity of water and collected upon a very small filter paper. The filter paper is dried, burned, the ignition carried to redness and afterwards cooled and weighed. In order to test the purity of the magnesia it is transformed into sulfate by the addition of a few drops of sulfuric acid. The excess of sulfuric acid is driven off by heating moderately by means of a gas-burner moving it in a circular manner round the bottom of the capsule and lifting the cover from time to time in order to allow the vapors of sulfuric acid to escape. The weight of the magnesium sulfate should correspond to that of the magnesia from which it was formed. The substitution of a gooch in place of the filter paper will render the above process more simple.

Magnesia exists most often in the soil in the state of carbonate or silicate. In this last state it is especially abundant in some soils, such as those which are derived from mica schists, serpentines, etc. In treating earth of this last quality with concentrated, nitric acid, there is dissolved also a notable part of the magnesia of the silicates. If, however, it is treated for some minutes only with dilute hydrochloric acid the amount of magnesia present as carbonate alone can be estimated separately.

410. **Method of the Halle Station.**[1]—For the estimation of magnesia the sample of soil or fertilizer is brought into solution in the same way as is given for the estimation of lime. After the separation of the silicic acid, the iron and alumina are precipitated in the presence of sodium acetate. In the case of phosphatic fertilizers, ferric chlorid should first be added in order that the excess of phosphoric acid shall be in all cases certainly combined with the iron. After this the lime is separated as usual with ammonium oxlate. After the precipitation of the lime, the magnesia is precipitated in an ammoniacal solution with sodium phosphate and the ammonium magnesium phosphate estimated exactly as in

[1] Bieler and Schneidewind, Die agrikultur-chemische Versuchsstation, Halle a/S, Berlin, 1892 : 85.

the case with the estimation of phosphoric acid, as magnesium pyro-phosphate.

A simpler method for the estimation of magnesia consists in precipitating it as ammonium magnesium phosphate in the presence of a solution of ammonium citrate, the other bases remaining in solution. In this case the operation is carried on in an inverse way as described under the estimation of phosphoric acid, the proper quantity of the acid solution being neutralized with ammonia and after the addition of sodium phosphate, the required quantity of citrate solution added and a further excess of ammonia supplied.

411. **Estimation of Manganese.**—The estimation of manganese in the presence of Fe_2O_3,Al_2O_3,CaO, etc., presents peculiar difficulties. In ordinary alluvial clays the quantity of manganese is proportionately small and its estimation may be neglected. In volcanic clays the quantity of manganese, in proportion to the lime and magnesia, is much larger. One of the methods used in France for estimating manganese is that of Carnot.[2] The hydrochloric acid extract of the soil is evaporated to dryness and heated with potassium bisulfate in order to destroy the organic substance, the neutralized solution of the residue precipitated with 20 cubic centimeters of hydrogen peroxid solution and 30 cubic centimeters of ammonia. The colorless filtrate gives, with nitric acid and bismuth peroxid, no trace of reaction for manganese. The precipitate, which includes the manganese as $5MnO_2$, MnO is washed by decantation, treated with oxalic acid and dilute sulfuric acid, and the excess of oxalic acid titrated with potassium permanganate in the usual way. Each five equivalents of available oxygen found corresponds to six equivalents of manganese.

412. **Estimation of Manganese by the French Method.**—Manganese exists in all plants and its presence in small quantities seems necessary to vegetation. The method of estimation adopted by the French Committee is the one proposed by Leclerc and is applicable even when the base exists in small quantities.

In 20 grams of the soil the organic matter is destroyed by incin-

[2] Comptes rendus, 1888, **107** : 997 and 1150.

eration. In a flask of 200 cubic centimeters capacity, are placed the sample and 30 cubic centimeters of water and, little by little, some hydrochloric acid for the purpose of decomposing the calcium carbonate. When effervescence has ceased ten cubic centimeters of the same acid are added and boiled for half an hour, filtered, washed, and the wash-water and filtrate evaporated to dryness in a porcelain dish. There are added 20 cubic centimeters of nitric acid of one and two-tenths density, and ten cubic centimeters of water. The liquor is boiled with constant shaking. Afterwards there are thrown in, in two or three portions, ten grams of lead dioxid. The boiling is stopped just at the moment when all the lead oxid is introduced into the liquor and the mixture is then shaken vigorously. The manganese is transformed by this treatment into a highly oxygenized compound having a deep rose coloration. It is transferred immediately afterwards to a graduated cylinder of 100 cubic centimeters capacity, with the wash-waters the volume is completed to 100 cubic centimeters and it is vigorously stirred in order to obtain a complete homogeneity of the liquid. The stirring rod is withdrawn and the liquid left to settle. At the end of some minutes the principal part of the liquid is clear, and it is decanted by means of a pipette graduated at 50 cubic centimeters, and this quantity of the clear liquid is poured into a small glass precipitating jar to which is added immediately, with constant stirring, a solution of mercurous nitrate from a graduated burette. The addition of the nitrate is arrested at the moment when the rose color of the liquor disappears, and the volume of the mercurous nitrate employed is read from the burette.

It is now necessary to determine the strength of the mercurous nitrate, that is the quantity necessary to decolorize one milligram of manganese. For this purpose dissolve by means of five cubic centimeters of hydrochloric acid 150 milligrams of manganese dioxid, which is prepared perfectly pure by means of precipitation. When the solution is complete evaporate to dryness, add one cubic centimeter of sulfuric acid and heat on a sand-bath until white fumes of sulfuric acid appear. Redissolve in water and make the volume up to 100 cubic centimeters. Each cubic centimeter of this solution should contain one milligram of manganese.

Treat five cubic centimeters of this solution, equivalent to five milligrams of manganese, in a capsule with 20 cubic centimeters of nitric acid and ten cubic centimeters of water, add ten grams of lead dioxid, carrying on the operation exactly as described above. Fifty cubic centimeters of the solution are decolorized by the solution of mercurous nitrate, and thus it is easy to calculate the quantity of manganese which corresponds to one cubic centimeter of the mercurous nitrate employed. By a simple proportion the quantity of manganese contained in the 20 grams of soil is calculated.

The mercurous nitrate is prepared by dissolving five grams of crystallized mercurous nitrate in one liter of water; it is allowed to repose for some time and is preserved in a well-stoppered flask.

413. **Estimation of Iron.**—Iron, in general, is quite abundant in the soil where it is met with, principally in the state of anhydrous sesquioxid or the hydrated sesquioxid of silicates. Some soils, however, only contain iron in small proportions and it can happen that the introduction of iron as a fertilizing element may be useful. Plants assimilate iron only in small quantities, but it appears to be indispensable to their development and to the proper functional activity of their assimilating faculties. The method of estimation which is recommended is based upon the decoloration of potassium permanganate by iron in the ferrous state. The following description, based on the method proposed by the French Committee, will illustrate the process to be followed.

Ten grams of the soil are ignited in a porcelain capsule until all organic matter is destroyed. The ignited mass is then introduced into a flask of 100 cubic centimeters capacity with 30 cubic centimeters of hydrochloric acid and 15 cubic centimeters of water. It is boiled for about half an hour. The iron oxid is dissolved and is found in solution in the form of ferric chlorid. After filtering and washing, the volume of the filtrate is reduced by evaporation to about 25 cubic centimeters. The liquor is afterwards placed in a flask of from 100 to 150 cubic centimeters capacity, which is closed by a stopper carrying a tube furnished with a valve destined to prevent the re-entrance of the air. Ten cubic centimeters of dilute sulfuric acid are added from a mixture

containing 20 cubic centimeters of strong acid and 80 cubic centimeters of water. Afterwards the iron is reduced to the ferrous state by introducing into the flask, in quantities of about five decigrams, metallic zinc and waiting after each addition until the portion last added is dissolved before adding another. This addition of zinc is continued until the iron is all reduced. When this point is reached and the last portion of zinc added is dissolved, the contents of the flask are transferred rapidly to a precipitating glass of about one liter capacity, in which there has been placed a little lately boiled but cold water. The flask is washed several times with cold water, previously boiled, to remove from it all traces of oxygen. The volume is made up to 500 cubic centimeters, and afterwards, without any loss of time, by means of a graduated burette and with constant stirring, a solution of potassium permanganate is added which is stopped exactly at the moment when the liquor begins taking on a light rose tint. The quantity of permanganate employed is read from the burette and is proportional to the amount of iron contained in the soil. A blank operation is made for the purpose of detecting traces of iron which the zinc may contain. If, as often happens, the soil contains a large amount of iron it is advisable to use only one gram of it for this operation. The aspect of the soil will indicate in general if it be very ferruginous, especially when the iron exists in the ferric state.

Preparation and Standardization of the Permanganate Liquor. —In one liter of water are dissolved ten grams of crystallized potassium permanganate and the quantity of iron which corresponds to one cubic centimeter of this liquor is determined. It may be well enough to remark that this liquor does not remain constant and it is necessary to titrate it from time to time. For this purpose pure piano wire may be used, being almost pure iron. One-tenth of a gram of this wire is dissolved in a flask in the manner recommended for treating the soil and with the same quantities of acid and water. When the solution is complete, it is transferred to the flask to be estimated, made up to one liter and permanganate added, just as in the case before mentioned, until the rose color persists. There is thus determined the quantity of iron which corresponds to each cubic centimeter of the permanga-

nate, and by a simple proportion, the quantity of iron contained in the soil analyzed is determined.

The Italian agricultural chemists proceed essentially in the same manner in determining the iron in soils, first igniting the sample and afterwards extracting the iron in the ferric state with boiling hydrochloric acid, reducing with hydrogen, and titrating with potassium permanganate.

The following are the reactions which take place:

$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O$.

$Fe_2Cl_6 + 2H = 2FeCl_2 + 2HCl$.

$10FeCl_2 + K_2Mn_2O_8 + 16HCl =$
$5Fe_2Cl_6 + 2KCl + 2MnCl_2 + 8H_2O$.

Sulfuric may take the place of hydrochloric acid in the above reactions.

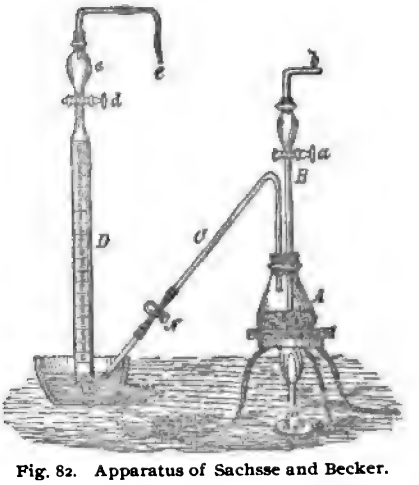

Fig. 82. Apparatus of Sachsse and Becker.

414. **Method of Sachsse and Becker.**[8]—Ferric oxid (not as silicate) in soils can be estimated by reducing with hydrogen, and measuring the hydrogen which is evolved by the action of the reduced iron on an acid. The sample of soil is weighed in a platinum boat, the boat put into a wide glass tube and heated in a stream of dry hydrogen. While this is going on, water is boiled in the flask *A* (see Fig. 82) from which the stopper has been re-

[8] Die landwirtschaftlichen Versuchs-Stationen, 1892, **41**, 453.

moved, to drive out the air. When the reduction of the ferric oxid is complete, the boat is slipped out of the tube into the flask without interrupting the hydrogen evolution. In order to accomplish this without allowing the reduced iron to come in contact with the air the flask is inclined, the end of the glass tube inserted until it is covered with water and the boat is then dropped beneath the water. The flask is closed with a cork provided with a funnel tube, *B*, and a delivery tube, *C*; the cock *a* is opened, and tube *b* connected with a carbon dioxid apparatus from which the gas is passed into *A* until all the air is displaced. This point is determined by filling the burette *D* with potash-lye by aspiration at *C* and allowing the escaping gas from *C* to enter the burette as indicated in the figure. Any residual gas in *D* is removed by aspiration at *C* and allowing the potash-lye in *e* to enter in its place. The end of the tube *C* is placed under the measuring tube *D*, and the clamp *f* opened and the cock *a* closed. The funnel above *B* is filled with dilute, boiled sulfuric acid, the cork of *b* replaced and again connected with the carbon dioxid apparatus. The burner under *A* is lighted and acid let in. By continued boiling, all the hydrogen is driven into *D*, the carbon dioxid accompanying it being absorbed. The measuring tube is placed in a tall cylinder of water, the volume of gas read and reduced to 0° and 760 millimeters barometric pressure. To be certain that all carbon dioxid is absorbed, some fresh potash-lye may be introduced into *D* by carefully opening *d*. The iron is then computed from the volume and weight of the hydrogen by the formula (1) $Fe + H_2SO_4 = 2H + FeSO_4$.

If the substance analyzed contains iron silicates, these may be partly decomposed with formation of ferrous sulfate, according to the reaction (2) $2Fe + Fe_2(SO_4)_3 = 3FeSO_4$. This will redissolve a part of the metallic iron and yield ferrous oxid. In this case the contents of the flask are cooled in an atmosphere of carbon dioxid, made up to 500 cubic centimeters, of which 250 cubic centimeters are quickly filtered and titrated with permanganate. In order to properly distribute the iron in harmony with its previously existing states the following computations may be made:

Represent the ferrous oxid corresponding to formula (1) by x
and that " " " (2) by z
and that found by titration with permanganate (3) by a.

We have then the equation $x + z = a$. Since 72 parts by weight of ferrous oxid formed by formula (1) evolve two parts by weight of hydrogen, x parts of ferrous oxid would set free $\frac{x}{36}$ parts of hydrogen; and this corresponds to the hydrogen found in the cylinder *D; viz.*, b.

If $\dot{a} = \frac{1}{36}$ then $\dot{a}\,x = b$ and by solving the equations we get $z = a - 36\ b$ and $x = 36\ b$. The ferrous oxid arising according to formula (2), however, is derived in such a way that only one-third of it corresponds to metallic iron. Then: $x + \frac{1}{3}\ z = \frac{1}{3}\ a + 24\ b$. For computing the total ferric oxid reduced by hydrogen there must, therefore, be added 24 parts by weight of hydrogen to one-third of the ferrous oxid found by titration with permanganate, and this quantity of ferrous calculated to ferric oxid. Some silicates, such as the micas, give ferrous oxid with hot dilute sulfuric acid. A correction for this is obtained by making one or more determinations without previously reducing with hydrogen.

The method of procedure above described appears to be capable of giving in an easily attainable manner some valuable indications of the state in which iron exists in a soil. While plants do not use any notable quantity of iron during their growth, nevertheless, its physiological importance is unquestioned. The chief points of difficulty to be considered are found in the changes which the iron may undergo even while heating in a stream of hydrogen, and the practical difficulties of obtaining carbon dioxid entirely free of air. The latter difficulty may be overcome by making blank experiments with carbon dioxid alone and estimating the volume of residual gas. The total volume of hydrogen obtained is then to be diminished by the ascertained amount.

In regard to the second point it is known that both ferrous and ferric oxids when ignited with hydrated silicates partly decompose and form new silicates. Care should therefore be taken not

to carry the temperature too high during the process of ignition.

415. Carnot's Method for Estimating Phosphoric Acid in Soils.—Carnot[4] proposes the following procedure for the estimation of phosphoric acid in soils. The principle of this method depends upon the isolation of silica by the double precipitation of phosphomolybdate.

Ten grams of the sifted soil, dried at 100°, are charred if organic matter be present. The charred mass is moistened with water and afterwards with nitric acid, until the carbonates are decomposed. The mass is digested with ten cubic centimeters of nitric acid for two hours at about 100°, with frequent stirring and the addition of fresh acid, from time to time, to replace that which has been evaporated. After filtering and washing with hot water the filtrate is evaporated to a volume of 50 cubic centimeters and treated with five cubic centimeters of concentrated nitric acid and half a gram of crystals of chromic acid. After covering the dish with a funnel to return condensed vapors its contents are heated to the boiling point for half an hour to complete the destruction of organic matter. At the end of this time five grams of ammonium nitrate are added to facilitate the precipitation of the phosphoric acid, and 50 cubic centimeters of molybdate solution and the mixture kept at a temperature of about 100° for an hour. The precipitate obtained is washed twice by decantation with water containing one-fifth of its volume of ammonium molybdate solution. It is dissolved in 30 cubic centimeters of ammonia diluted with an equal bulk of warm water. The solution and the washings should measure 80 cubic centimeters and the ammonia therein is neutralized with nitric acid, keeping the temperature below 40°. When the yellow precipitate formed ceases to redissolve on stirring, that is when the ammonia has been neutralized, a mixture of three cubic centimeters of pure nitric acid and five cubic centimeters of water is added, together with the same quantity of molybdate solution. After standing for two hours at 40° the precipitate is brought upon a filter, washed first with water containing one per cent of nitric acid, and finally with a little pure water, and dried at 100° and weighed. A slight reduction of the phosphomolybdate, indicated by a blue tint

[4] Buletin de la Société chimique de Paris, 1893, [3], **9** : 343.

when its edges come in contact with the filter paper may be neglected. The weight of the precipitate mutilplied by the factor 0.0373 gives the quantity of phosphoric acid. The object of the second precipitation is to relieve the process of the necessity of rendering the silica insoluble, as the presence of silica in the solution as above treated does not interfere with the complete precipitation of the phosphate. This was proved by the author, by the introduction of considerable quantities of sodium silicate and these were found not to interfere with the accuracy of the operation.

The results are as accurate as those obtained by the methods of the consulting committee of the agricultural stations. The coefficient employed; *viz.*, 0.0373, is not the same as that recommended by the committee; *viz.*, 0.043. The committee, however, itself has recognized the inaccuracy of the latter number. The composition of the compound obtained by double precipitation according to Carnot is $P_2O_5 24MoO_3 3(NH_4)_2O + 3H_2O$.

416. Citrate Method of the Halle Experiment Station.—The available or easily soluble phosphoric acid in soils is estimated by Maercker and Gerlach, as follows:[5]

Sixty grams of the air-dried soil as prepared for analysis, are placed in an erlenmeyer with 300 cubic centimeters of two per cent citric acid solution and digested for 24 hours in the cold. It is necessary in this time to shake the flask four or five times and to put the stoppers in loosely in order to allow the escape of any evolved carbon dioxid. Of this mixture 200 cubic centimeters are filtered and evaporated in a 300 cubic centimeter dish to dryness. There remains, in most cases, a syrupy-like mass from which even by strong heating the silica is not completely separated. In order to reach this result the residue is treated with 20 cubic centimeters of concentrated sulfuric and five cubic centimeters of fuming nitric acid and heated over a bunsen. As soon as the appearance of foam denotes the beginning of the reaction the lamp must be removed. With strong foaming and the evolution of red-brown vapors the citric acid is completely oxidized. After the reaction is ended the contents of the dish are heated for

[5] Die Agrikultur-Versuchs-Stationen, Halle, a/S, Berlin, 1892 : 70.

about 15 minutes over a small flame so that a continuous, yet not too violent evolution of sulfuric acid fumes takes place. After the silicic acid and the greater part of the lime have been rendered insoluble in this way the contents of the dish are diluted with water, stirred with a glass rod, washed into a 200 cubic centimeter flask, cooled, filled up to the mark, and filtered. From the filtrate, 100 cubic centimeters, corresponding to 20 grams of the sample are made slightly alkaline with ammonia, acidified by a few drops of hydrochloric acid, and after cooling treated with 50 cubic centimeters of the standard citrate of ammonia solution and 25 cubic centiemters of the standard magnesia mixture. The complete separation of the precipitate requires about 48 hours and shaking of the precipitate is not necessary. The incineration and weighing of the precipitate are conducted in the usual manner.

417. **Estimation of Phosphoric Acid in Soils Soluble in Strong Acids.**—The method of separating phosphoric acid directly in the presence of citrate of ammonia is regarded by the chemists of the Halle Station as incomparably more convenient than the older and more generally used process. At the Halle Station 25 grams of the soil sample are boiled with 20 cubic centimeters of nitric acid and 50 cubic centimeters of concentrated sulfuric acid for half an hour. With very clayey soils only half the quantity of the sample mentioned above is used in order to avoid the too great accumulation of soluble alumina. The oxidation of the organic substances of the soils must be carried on at a moderate heat to avoid foaming. During the boiling, the flask is to be often shaken to prevent the soil constituents from accumulating too firmly at the bottom. The total volume is finally made up to 500 cubic centimeters.

For the estimation, 100 cubic centimeters of the solution, corresponding to five (or two and a half) grams of the soil, are used. In order to nearly completely saturate the acid, the solution is treated with 20 cubic centimeters of 24 per cent ammonia, care being taken that the precipitate of iron and alumina which is formed is again completely dissolved. The solution is cooled and treated with 50 cubic centimeters of the citrate solution, and then

with 20 cubic centimeters of ammonia of above strength, and precipitated with the magnesia mixture. The filtration of the precipitate should not be made for at least 48 hours, during which time the flask should be often shaken to prevent the attachment of ammonium magnesium phosphate to its sides and bottom.

A detailed description of the citrate method for estimating phosphoric acid will be found in the chapter devoted to this subject under fertilizers in Volume Second.

418. French Method for Phosphoric Acid.—Phosphoric acid is found in the soil principally in combination with alumina and iron oxid, with organic matters, or with lime and magnesia. Whatever may be the state in which it is found all the phosphoric acid, with the exception of that which enters into the constitution of insoluble mineral particles, can be brought into solution by acids and determined by some of the approved methods. This method of solution, therefore, is capable of determinating very accurately the total proportion of phosphoric acid in the soil, but it is incapable of rendering account to us of the state in which the phosphorus is found and of its aptitude to be utilized by plants.

The estimation of soil phosphorus, as recommended by the French Committee, is carried on in the following way.[6] Twenty grams of the earth are submitted to ignition in a muffle heated to the temperature of redness but not higher. This calcination eliminates the organic materials, whose intervention in subsequent reactions might be able to prevent the precipitation of a part of the phosphoric acid. The calcined earth is placed in a dish of about 11 centimeters diameter and saturated with water. There is then added in small quantities, as long as effervescence is produced, nitric acid of 36° Baumé. When the effervescence has ceased, after thorough shaking and the addition of a new quantity of acid, it will be found that the whole of the calcium carbonate in the soil has been decomposed. It is necessary then to proceed to the solution of the phosphoric acid by adding 20 cubic centimeters of nitric acid and heating on the steam-bath for five hours, shaking from time to time, and avoiding complete desiccation. At the end of this time the whole of the phosphoric acid has entered into

[6] Annales de la Science Agronomique, 1891, 1 : 267.

solution. It is taken up by warm water, filtered, and the insoluble residue washed with small quantities of boiling water. But from the solution obtained, which holds in addition to phosphoric acid, some oxid of iron, alumina, lime, magnesia, etc., it is necessary to separate the silica which has passed into solution. For this purpose the mass is evaporated to dryness on a sand-bath, heating toward the end of the operation with precaution and not allowing the temperature to pass beyond 110°-120°. In these conditions there is obtained a magma which sometimes remains quite syrupy when the earth is very highly impregnated with calcium carbonate, but in which the silica is insoluble. It is indispensable that it be eliminated wholly because it would introduce grave errors into the results, as will be seen later on. If the temperature be carried too high during the desiccation this silica would react upon the earthy salts and alkaline earths forming silicates and it would be found ultimately again in solution. The application of a too high temperature would also render somewhat insoluble in nitric acid the iron and aluminum oxids, and these would retain small quantities of phosphoric acid. The desiccation, therefore, requires to be conducted with great precaution. When it is accomplished there are placed in the dish five cubic centimeters of nitric acid and five cubic centimeters of water, and the whole heated on the sand-bath until the entire amount of iron oxid is dissolved. The solution is filtered and washed with small quantities of boiling water in such a way that the total volume of the filtrate will not exceed from 25 to 35 cubic centimeters. Afterwards there are added 20 cubic centimeters of ammonium nitromolybdate and the whole is left at rest for 12 hours at the ordinary temperature. At the end of this time the phosphoric acid is precipitated in the form of ammonium phosphomolybdate. In order to be certain that an excess of nitromolybdate has been used in the precipitation, which is indispensable to the total precipitation of the phosphoric acid, a few cubic centimeters of the filtrate are removed by means of a pipette and are mixed with their own volume of the ammonium nitromolybdate. If, at the end of an hour or two, no precipitate is formed the operation can be regarded as terminated.

In order to collect and weigh the ammonium phosphomolyb-

date some precautions are necessary. Two smooth filters are used, one of which serves as a counter-weight for the other on the balance. After bringing the free contents of the dish onto the filter the part of the phosphomolybdate adhering to the dish is detached by the aid of a stirring rod, one of the ends of which is covered with a piece of rubber tubing. The washing is accomplished with very small quantities of water containing five per cent of its volume of nitric acid. When all of the precipitate is collected upon the filter and the washing is terminated a few drops of water are thrown upon the upper borders of the filters to displace the acid liquor which has been used in washing. The filters are then carried to the oven where they are dried at a temperature not exceeding 90°. The application of a higher temperature would decompose the ammonium phosphomolybdate and lead to results which would be too low. After the drying is completed the two filters are separated and placed upon the pans of the balance and the weight of the ammonium phosphomolybdate ascertained. This, multiplied by the coefficient 0.043, (0.0373 see page 453) gives the quantity of phosphoric acid contained in the weight of the soil which has been employed. The ammonium phosphomolybdate is pure if all the silica has been eliminated, but if a part of that has remained in solution it would furnish an ammonium silicomolybdate whose weight would be added to that of the phosphomolybdate. The elimination of the silica, therefore, should be made with the greatest care.

Different processes have been proposed in order to determine the forms under which phosphoric acid should be regarded as most assimilable. This problem is fully discussed elsewhere. The solubility of phosphoric acid in these different reagents gives information in regard to its state, but the relations which exist between this solubility and the assimilability of the acid can only be determined by comparisons with pot and field experiments.

Preparation of the Ammonium Nitromolybdate.—One hundred grams of molybdic acid are dissolved in 400 grams of ammonia of a density of 95. The mixture is filtered, and the filtered liquor is received drop by drop in 1,500 grams of nitric acid of one and two-tenths density, constantly stirring. This mixture is left standing for some days in an unexposed locality, during

which time a deposit is formed. The clear part is decanted and used.

The above method of the French chemists unfortunately attempts to determine the phosphorus content of the soil by weighing the yellow precipitate and using an empirical factor for the calculation, a factor which is probably too high.

Experience has shown that at this point it is far more accurate to continue the process by dissolving the yellow precipitate, and subsequently obtaining the phosphoric acid in combination with ammonia and magnesia, or according to the process of Pemberton the content of phosphoric acid in the yellow precipitate may be determined by titration. In regard to the latter method which will be given in full in Volume Second, it may be said that it has been found quite accurate by several analysts, although it is important that a precipitate which is so variable in its constitution should be secured under standard conditions in order to secure an exact determination by titration.

419. Petermann's Method for the Estimation of the Phosphoric Acid Soluble in Alkaline Ammonium Citrate.[7]—From 25 to 50 grams of the sample of soil are titrurated with 100 cubic centimeters of alkaline ammonium citrate and placed in a flask of 250 cubic centimeters capacity, and allowed to digest for one hour at a temperature of from 35°-40°. The citrate solution is made as follows: Dissolve 500 grams of citric acid in concentrated ammonia of 0.92 density in sufficient quantity to secure a neutral reaction. The solution is reduced to a density of 1.09 at 15°, and there is added for each liter thereof 50 cubic centimeters of strong ammonia (0.92 specific gravity). After cooling the soil solution mentioned above, make up to the mark, filter, evaporate 200 cubic centimeters of the filtrate to dryness on a sand-bath in a platinum dish, burn lightly at first, and afterwards at a higher temperature. Take up the residue of the incineration with water and about two cubic centimeters of nitric acid, heat a few minutes gently, filter into a bohemian flask and precipitate with 50 cubic centimeters of ammonium molybdate solution in nitric acid, and estimate the phosphoric acid in the usual way.

[7] L'Analyse du Sol, Brussels, 1891 : 20.

420. Method of Dyer for Total and Assimilable Phosphoric Acid.[8]—For the determination of phosphoric acid, soluble in citric acid, secured as described in paragraph 367, 500 cubic centimeters of the filtrate obtained, corresponding to 50 grams of the soil, are evaporated to dryness in a platinum dish, gently ignited, dissolved with hydrochloric acid, again evaporated, redissolved and filtered, and the phosphoric acid determined below as in the method applied to the hydrochloric acid extract of the soil itself.

The total phosphoric acid soluble in strong acids is determined in each case in ten grams of the dried soil and also in 25 grams, the mean of the two results being taken. The numbers obtained in each case are, however, all but identical, the difference in the duplicate percentages being in most cases, only a small one in the third place of decimals.

The soil is incinerated and digested with hydrochloric acid, and evaporated to dryness, redigested with acid, filtered, and washed. The filtrate and washings are concentrated to a small bulk, and treated, in the cold, with excess of a solution of ammonium molybdate in nitric acid. After standing 48 hours, the liquor is decanted through a filter, the precipitate washed several times by decantation, first with one per cent nitric acid, then with pure water in very small doses, and finally transferred to the filter and washed free from excess of acid. The ammonium phosphomolybdate is dissolved in ammonia, evaporated to dryness in a platinum capsule, adding water once or twice, and dried to constant weight at 100°. The residue contains three and one-half per cent of its weight of phosphoric acid. This is the method of Hehner; and for determining small quantities of phosphoric acid, such as occur in soils or in solutions of iron and steel, is in the opinion of Dyer very much to be preferred to the old-fashioned method of conversion into magnesium ammonium phosphate. The solubility of the yellow precipitate in the small quantity of wash-water used is in most cases negligible. As a matter of fact, the quantity of wash-water used in these analyses was found capable of dissolving only 0.005 gram of precipitate, of which only 0.00017 is phosphoric acid, making an error of 0.0017 per cent on the soil if ten grams be used, or of only 0.0006 if 25 grams be used. In the citric acid

[8] Journal of the Chemical Society, Transactions, 1894, **65** : 140.

experiments the solution from 50 grams of soil is used, when the error due to solubility of precipitate shrinks to 0.0003 per cent. The correction for this solubility is, however, made in each case.

It may be observed that the method of Hehner is not applicable if the molybdic solution be added to a hot liquid, since, in that case, some molybdic acid is sure to crystallize with the yellow precipitate. Moderate and careful warming to about 35° hastens precipitation, but it is preferable, when speed is not a special object, to precipitate cold, and leave the beaker standing at the laboratory temperature over night, or longer if the quantity to be determined is very minute. The objections to heating a soil before the extractions of its easily soluble constituents have already been pointed out and apply also to the above process.

421. **Methods of Berthelot and André.**[9]—The phosphorus in the soil may be found under four forms; *viz.*,

1. Phosphoric acid in phosphates.
2. Phosphoric acid in compound ethers similar to phosphoglycerates which dilute acids and alkalies decompose slowly with regeneration of phosphoric acid.
3. Mineral compounds of phosphorus of the order of phosphites and hypophosphites which are resolved by oxidizing solutions like nitric acid with formation of phosphoric acid but which are only oxidized to this state by the reagents employed after a contact of indefinite length and uncertainty.
4. In the form of organic compounds of the order of the oxid of triethylphosphine, phosporated phenyl compounds and cerebric acid. These compounds are transformed into phosphoric acid with extreme difficulty by the usual reagents employed in the wet way.

It is, therefore, seen that the promiscuous employment of oxidizing agents for the valuation of phosphoric acid in soils and vegetables is not a very reliable procedure. The same is true after incineration by which more or less phosphorus may be lost or rendered insoluble in acids. For analytical purposes the phosphorus is assumed to exist in the three special forms mentioned

[9] Annales de Chimie et de Physique, 1888, [6], **15** : 128.
Berthelot, Chimie végétale et agricole, Paris, 1899, **4** : 83.

below. The methods used by Berthelot and André for the estimation of these forms of phosphorus are as follows:[10]

Total Phosphorus.—The sample is at first oxidized by a current of air near a red heat and the vapors are conducted over a column of sodium or potassium carbonate at the same temperature. The combustion is finished in a current of pure oxygen. All phosphorus compounds, even those which are volatile, are by this treatment converted into phosphoric acid. The part of the acid held by the carbonate is to be determined with the non-volatile portions.

A less certain method of oxidation consists in mixing the material with potassium nitrate and carefully throwing it little by little into a red hot platinum crucible.

Estimation of the Phosphoric Acid Pre-existing as Phosphates.—The sample is treated with a cold dilute acid incapable of exercising an oxidizing or decomposing effect on the ethers. The dissolved phosphoric acid is precipitated and weighed in the usual way. The precipitate first obtained should be ignited and the phosphoric acid taken up and reprecipitated. This is necessary to remove any organic matter or silica which the first precipitate may contain.

Estimation of Ethereal Phosphoric Acid.—The sample is boiled for some time with a non-oxidizing acid or with a concentrated solution of potash. The phosphoric acid dissolved represents that which was present as phosphates and as ethers. From this, deduct that portion pre-existing as phosphates, ascertained as above, and the remainder represents the part derived from the ethereal compounds.

Estimation of Phosphorus in Organic Compounds and Special Minerals.—From the total phorphoric acid deduct that found as phosphates and ethers. The difference represents the quantity combined as noted in the caption. Illustration.

A sample of soil contained:

	Per cent.
Total phosphoric acid	0.292
Of this, pre-existing as phosphoric acid	0.109
As ethereal phosphoric acid	0.074
As organic phosphoric acid	0.109
Sum	0.292

[10] Annales de Chimie et de Physique, 1892, [6], **25** : 303.

422. **Method Used at the Riga Station.**—In the method pursued at the experimental station at Riga[11] the organic matter in the fine earth is first destroyed by igniting 25 grams in a muffle. The ignited residue is placed in a 250 cubic centimeter erlenmeyer and digested with 150 cubic centimeters of ten per cent hydrochloric acid for 48 hours with frequent shaking. The filtrate is evaporated to dryness in a porcelain dish to separate any dissolved silica, the residue taken up with dilute hot nitric acid, filtered, and the phosphoric acid precipitated with nitro-ammonium molybdate. The final weighing is made as magnesium pyrophosphate, following the usual procedure in respect of precipitation and washing. Experiments show that approximately 95 per cent of the phosphoric acid is obtained by one extraction and five per cent by a second, conducted exactly as the first. Thoms draws the following conclusions from a long series of determinations:

(1) For the simple purpose of determining the need of a soil for phosphatic fertilizer a single extraction with ten per cent hydrochloric acid is sufficient. The difference between the first and second extraction; *viz.*, from five to six per cent is too small to be of any value from a practical point of view.

(2) A soil which has been ignited until organic matter is destroyed gives up to the hydrochloric acid solvent about 14 per cent more phosphoric acid than a non-ignited sample would. This is in accord with the experience of the Bureau of Chemistry which shows that heating increases the solubility of some of the mineral ingredients of soil.

(3) The mean temperature in the flask during extraction on a steam-bath is 74°.

423. **Method of Hilgard.**[12]—A suitable quantity of soil (usually from three to five grams) is ignited in a platinum crucible, care being taken to avoid all loss. The loss of weight after full ignition gives the amount of chemically combined water and volatile and combustible matter.

The ignited soil is now removed to a porcelain or glass beaker, treated with four or five times its bulk of strong nitric acid, di-

[11] Thoms, Zur Wirtschätzung der Ackererden, Second Contribution, Riga, 1893 : 114.

[12] Bulletin No. 38, Division of Chemistry : 80.

gested for two days, evaporated to dryness, first over the water-bath and then over the sand-bath, moistened with nitric acid, heated and treated with water. After standing a few hours on the water-bath it is filtered and the filtrate is evaporated to a very small bulk (ten cubic centimeters) and treated with about twice its bulk of the usual ammonium molybdate solution, thus precipitating the phosphoric acid. After standing at least 12 hours, first at a temperature of about 50°, the precipitate is collected on a filter and washed with a solution of ammonium nitrate acidified with nitric acid. The washed precipitate is dissolved on the filter with dilute ammonia water. After washing the filter carefully, the ammoniacal solution is treated with magnesia mixture, by which the phosphoric acid is precipitated. After allowing it to stand 24 hours the precipitate is brought onto a filter, washed in the usual way, dried, ignited, and weighed as magnesium pyrophosphate, from which the phosphoric acid is calculated. When a gelatinous residue remains on the filter after dissolving the phosphomolybdate with ammonia it may consist either of silica not rendered fully insoluble in the first evaporation, or, more rarely, of alumina containing phosphate. It should be treated with strong nitric acid, and the filtrate with ammonium molybdate; any precipitate formed is, of course, added to the main quantity before precipitating with magnesia solution.

424. Separation of Phosphoric Acid from Iron and Alumina.— The following methods are among the first of the exact methods suggested for the complete separation of the phosphoric acid from the iron and alumina in soil analysis, where large quantities of these bases are found in solution:[13]

1. After the separation of the greater part of the iron and alumina the phosphoric acid is precipitated from the solution in nitric acid by molybdic acid. The process is carried on as follows:

The acid extract is heated in a flask to boiling and the remaining ferric oxid completely reduced by the gradual addition of small particles of sodium sulfite. While still warm the free acid is neutralized with soda-lye, and ammonia added until the fer-

[13] Zeitschrift für analytische Chemie, 1864, 8 : 94.

rous hydroxid and the aluminum hydroxid are completely separated. Acetic acid is added in excess and until about four-fifths of the whole precipitate have passed again into solution. Then, after boiling for a moment, the whole is quickly filtered through a large filter with a cover, and the contents of the filter finally washed slightly. All the phosphoric acid is thus obtained in combination with some alumina and a very little iron. Nearly the whole of the iron and the larger part of the alumina, by this precipitation, are found in the filtrate and therefore cannot disturb the estimation of phosphoric acid in succeeding portions. The filter is filled with boiling water and a little nitric acid added and the dissolved precipitate is received in a beaker. The precipitation of the phosphoric acid is then accomplished by ammonium molybdate in the presence of nitric acid. After 24 hours all the phosphoric acid is thus precipitated and the precipitate is free from iron.

2. In the method of Schulze[14] the iron is completely, and the alumina, with the exception of a small quantity, separated, and the precipitation of the phosphoric acid is accomplished either by the addition of a small quantity of tartaric acid and afterwards magnesium sulfate, or directly when it is desired to avoid the use of tartaric acid by means of ammonium molybdate. The principle of the separation of the iron and alumina depends on the fact that when the hydrochloric acid solution is nearly neutralized with soda or ammonia, and boiled after treatment with ammonium formate, the greater part of the alumina remains in solution, while the iron and phosphoric acid are precipitated. The precipitate is quickly filtered, washed with hot water, dried, taken from the filter and fused in a silver crucible with pure caustic alkali, either soda or potash. On solution and boiling with water, the iron is completely separated from the phosphoric acid, and from the small quantity of the alumina present and the precipitation of the phosphoric acid can now be accomplished, either by saturation of the alkaline solution with hydrochloric acid and the direct addition of the magnesia solution after the addition of a

[14] Zeitschrift für analytische Chemie, 1864, **3** : 94.
Chemisches Centralblatt, 1861 : 3.

little tartaric acid and ammonia, or after the addition of nitric acid by ammonium molybdate.

In connection with this method of treatment attention is called to the fact that simple incineration of a compound containing organic phosphorus is not sufficient to secure all the phosphorus as phosphoric acid.

425. Matters Soluble in Sulfuric Acid.—It will have been noticed that of mineral acids, hydrochloric and nitric have been most frequently proposed as solvents for soil. Sulfuric acid has some advantages as a solvent, being in many respects more regular in its action and more sure in its results than those usually employed. When employed with a little mercury the organic matter contained in the sample is completely destroyed usually at the end of an hour. Moreover, the true clay (argile) is completely dissolved at the end of two hours, and any lime present is rapidly transformed into sulfate.[15] Only the silica and certain of the silicates will resist the action of the acid. Hence, by a three hours digestion of the soil at a boiling temperature all of the fertilizing elements of the sample pass into solution, while those elements unimportant as plant foods remain undissolved. The heating of the sample is begun at a low temperature, when any sulfurous acid that may arise from the reducing action of the organic matter will be given off. The heat is gradually increased with frequent shaking of the flask to avoid caking until the sulfuric acid begins to boil, usually about an hour. The boiling should be continued for three hours. In the dissolved part of the sample are found the total nitrogen, phosphoric acid, potash, soda, lime, magnesia and iron. It is better, however, to treat a second portion of the sample with acetic acid to obtain the lime and magnesia. The estimation of the dissolved constituents of the soil is conducted by any of the standard methods. This process is much like that of Goss.

426. Method of Goss.—On account of the length of time required to determine the phosphoric acid in soils by the usual methods, Goss[16] has proposed the following modification which in his hands has given satisfactory results:

[15] Aubin and Alla, Encyclopédie chimique, **4** : 174.

[16] Bulletin No. 43, Division of Chemistry : 58.

Place ten grams of the air-dried soil, which has been sifted through a one millimeter-mesh sieve in a pear-shaped, straight necked, kjeldahl digestion flask, which has been marked to hold 250 cubic centimeters. Add approximately seven-tenths gram of yellow mercuric oxid and from 20 to 30 cubic centimeters of concentrated sulfuric acid, as for the determination of nitrogen. Twenty cubic centimeters of acid are nearly always sufficient, but in the case of unusually finely divided clay soils containing little or no sand it is necessary to use 30 cubic centimeters to prevent caking of the contents of the flask. In doubtful cases 20 cubic centimeters of acid should first be added and at the end of five or ten minutes, if the contents show a tendency to cake, ten cubic centimeters more should be introduced. Thoroughly mix the contents of the flask by shaking, place on a suitable support over a burner, boil for one hour, cool, add about 100 cubic centimeters of water, five cubic centimeters of concentrated hydrochloric acid, and two cubic centimeters of concentrated nitric acid, boil gently for two minutes to oxidize iron, cool, make up to volume and filter through a dry folded paper until perfectly clear. In order to secure a clear filtrate it will usually be found necessary to pour the first portion of the filtrate back through the paper three or four times. Transfer 100 cubic centimeters of the filtrate to an ordinary flask of about 450 cubic centimeters capacity, add strong ammonia until a permanent precipitate forms, then six or eight cubic centimeters of nitric acid to dissolve the precipitate, and boil until clear. In the case of many soils it is not absolutely necessary to oxidize with hydrochloric and nitric acids, as a clear solution can be secured at this point without further oxidation. In the case of some soils, however, and especially in subsoils, the solution cannot be cleared up even by prolonged boiling with nitric acid, but if the solution have been previously oxidized, a clear solution can be secured without any difficulty whatever. Remove the flask from the lamp and after two minutes add 75 cubic centimeters of molybdate solution, place the unstoppered flask in an open water-bath kept at a temperature of 80° for 15 minutes, shaking vigorously four or five times while in the bath; then remove, let stand ten minutes to allow the precipitate to settle, filter through a nine centimeter filter avoiding too strong a pressure at

first, wash the flask and precipitate thoroughly with ammonium nitrate solution, place the flask in which the precipitation was made under the funnel, shut off the vacuum and close all the valves to the filtering jar to form an air-cushion and prevent too rapid filtration, fill the filter two-thirds full of hot water, add a few cubic centimeters of strong ammonia, and aid solution, if necessary, by stirring the precipitate with a small glass rod.

As pointed out by Hilgard, aluminum is sometimes carried down with the phosphoric acid upon precipitating with molybdate solution, in which case some of the phosphoric acid will not be dissolved in the treatment with ammonia. This will be indicated, first, by the appearance of a white precipitate upon dissolving the yellow precipitate in ammonia; and, second, by the difficulty experienced afterward in washing. If such a precipitate be present in any appreciable quantity, proceed as follows:

After washing out all the ammoniacal solution in the usual manner, place a small beaker under the funnel, close all valves, fill the filter one-third full of hot water, add the same amount of concentrated hydrochloric acid, and receive the solution and washings in the flask used for the former precipitation with molybdate solution, add 20 cc. of strong ammonium nitrate solution, neutralize with ammonia, clear up the solution with nitric acid, precipitate with 50 cc. of the molybdate solution, as before. Filter and wash the yellow precipitate as before, dissolve in ammonia, and add to the first portion. A third treatment may sometimes be necessary. As soon as the yellow precipitate is dissolved open the valve to the filtering jar but do not turn on the pump; after the solution has all passed through rinse the filter once with a small amount of hot water; after the last portion has passed through remove the flask and place a lipped beaker under the funnel and heat the solution in the flask to boiling. If the solutions have not been oxidized, a blue color is sometimes present upon dissolving the yellow precipitate in ammonia. This can be discharged by boiling the ammoniacal solution for a minute or two and shaking at the same time. Again pour the solution through the filter, avoiding use of the pump at first, otherwise loss from spattering is likely to ensue, wash out the flask and filter with a small amount of hot water, (the total filtrate should not

exceed 50 cubic centimeters), add hydrochloric acid to the contents of the beaker while hot, until the yellow color appears, then add a few drops of ammonia until the solution clears, cool, add an excess of filtered magnesia mixture from a burette, a drop at a time with constant stirring, let stand 15 minutes, add 20 cubic centimeters of strong ammonia specific gravity 0.90, let stand over night, filter, wash the precipitate with dilute ammonia, dry, ignite intensely over blast-lamp for ten minutes, cool in desiccator and weigh the $Mg_2P_2O_7$ secured.

Time of Digestion.—Experience has shown that very little phosphoric acid is extracted from the sample by digestion with sulfuric acid after the first 30 minutes.

Time Required to Precipitate Phosphomolybdate.—When the yellow precipitate is obtained according to the method of Goss practically the whole of it will be thrown down in five minutes.

Agreement with Standard Methods.—Comparative tests of the Goss method against standard methods have shown that it gives almost identical results with them. The variations were never more than from 0.02 to 0.03 per cent.

While this method has not been sufficiently tried to receive unconditional recommendation it possesses merits which entitle it to the attention of analysts. The method of preparing the reagents is the same as described in volume second of this work in the official method of determining phosphoric acid.

427. Volumetric Method of Estimating Phosphoric Acid in Soils.—The principles which underlie the volumetric method of determining phosphoric acid will be discussed in full in volume second of this work. The method as applied to soils has been worked out by Williams.[17] The soil extract is prepared by any of the methods already described, and in all cases especially when organic acids or salts are used in the extraction, the organic matter must be destroyed, either by oxidizing agents, or where great quantities are present as is the case when organic solvents are employed, by evaporation to dryness and ignition. After dissolving and filtering the residues after the organic matter is removed

[17] Bulletin No. 119, North Carolina Agricultural Experiment Station: 279.

they are made up to known volume and portions equivalent to from one to 20 grams of the soil, according to the quantity of phosphoric acid present, removed for analysis.

In all cases the phosphoric acid is obtained by precipitation with a molybdate solution and washed free of any adhering acid. The precipitate (and adhering filter) is titrated directly with potassium hydroxid in excess and the remaining alkali determined by titrating with nitric acid using phenolphthalein as indicated. The details of the process are found under phosphoric acid in volume second. Excellent results comparable in accuracy with those obtained by the gravimetric method can be secured by this method in the hands of an experienced analyst, and it secures a great saving of time, especially when large numbers of analyses are to be done. It is considered especially applicable to those analysis where small quantities of phosphoric acid are involved.

428. Estimation of the Sulfuric Acid.—Sulfuric acid is generally present in small proportions in soils. Since the plants have need of sulfur it is proper to inquire into the presence of the compound which is its principal source. It is in combination with lime that sulfuric acid almost always exists. In addition to this there is also some sulfur combined with the organic matter of the soil.

By digesting a soil for six hours with hot, concentrated nitric acid the sulfates are dissolved, and there is transformed into sulfuric acid an important part of the sulfur which is combined with the humic substances. The quantity of soil to be operated upon should be about 50 grams.

After filtering and washing with hot water the filtered liquor is collected, in the French Committee method, in a flask and carried to boiling, and five cubic centimeters of a saturated solution of barium chlorid or sufficient to be in slight excess are added. The boiling is continued for some minutes and the flask is allowed to stand for 24 hours. The filtrate is received upon a filter and washed with boiling water, the filter dried and incinerated, allowed to cool, and as there may have been a slight reduction of the sulfate a few drops of nitric acid are added and a drop of sulfuric acid. It is now evaporated to dryness on a water-bath,

heated to redness for a few moments, cooled and weighed. The weight of the barium sulfate multiplied by 0.3433, gives the quantity of sulfuric acid obtained from the 50 grams of soil.

If it is desired to estimate only the sulfur which exists in the form of sulfate it is necessary to treat the soil with hydrochloric acid in a very dilute state, heating for a few moments only and afterwards precipitate by barium nitrate. If, on the other hand, it is desired to estimate the total sulfur which is sometimes of great interest, it is necessary to employ the process of Berthelot and André.

429. **Method of Berthelot and André.**—Sulfur may exist in the soil in three forms; *viz.*,

1. Mineral compounds, consisting generally of sulfates and in exceptional cases in marshy localities of sulfids of the metals and hydrogen sulfid.

2. Sulfur, existing in ethereal compounds or their analogues, as in urine, and mustard.

3. Organic compounds containing sulfur.

Estimation of Total Sulfur.—The principle on which this operation, as described by Berthelot and André, rests is that already described for phosphorus; *viz.*, oxidation in a current of oxygen and passing the vapors over a column of alkaline carbonate at or near a red heat.[18]

The ordinary methods of oxidation in the wet way give generally inexact results.

Estimation of Sulfur Pre-existing as Sulfates.—The sample is treated with cold, dilute hydrochloric acid. The filtrate is treated with barium chlorid, the precipitate collected, dried, ignited, to remove organic matter, washed with a mixture of sulfuric and hydrofluoric acids to remove silica, and afterwards weighed as barium sulfate.

Estimation of Sulfur as Sulfids.—Sulfur occurs in this state very seldom and usually reveals its presence by the characteristic order of hydrogen sulfid. The sample is distilled with dilute hydrochloric acid, and the hydrogen sulfid produced is made to pass through an acidulated solution of copper sulfate in such a way

[18] Annales de Chimie et de Physique, 1892, [6], **25** : 305.
Berthelot, Chimie végétale et agricole, Paris, 1899, **4** : 70.

as to transform the sulfur in the hydrogen sulfid into a sulfid, which is afterwards collected and weighed in the usual way. The use of a titrated solution of iodin is not advisable on account of the organic matter which may be present.

Estimation of Sulfur in Ethereal Compounds.—These compounds can be decomposed by boiling with a solution of potash or concentrated hydrochloric acid. The resulting sulfuric acid is precipitated with barium chlorid. Subtract from the sulfates thus obtained those pre-existing as sulfates; the difference represents the sulfur present in ethers.

Estimation of Sulfur in Other More Stable Organic Compounds.—This is estimated indirectly by subtracting from the total sulfur that present as sulfates, sulfids, and ethers.

430. **Method of van Bemmelén.**—As van Bemmelén[19] observes, the estimation of sulfuric acid in soils presents a number of difficulties. A small part of it can be present as sulfate insoluble in water. In addition to this, there is always some sulfur in the organic bodies present. If the soil is extracted with water then the sulfuric acid can be estimated therein if only a trace of humus substance has gone into solution. On the contrary, if there is much humus substance in solution, and also iron oxid, as is the case when the extraction is made with hydrochloric acid, then both of these must be removed, otherwise the estimation is very inexact. By fusing the residue of the solution with sodium carbonate and a little potassium nitrate the organic substance is destroyed, and after treatment with water the iron oxid is separated. If any sulfur has been dissolved in the organic substance present, this is then oxidized to sulfuric acid. The estimation of the sulfuric acid and of the sulfur, therefore, remains unsatisfactory.

In a sample of clay from Java, which was rich in calcium carbonate, but which contained no basic iron sulfate, there was found the following percentages of sulfuric acid:

Exhausted in the cold with very weak hydrochloric acid, 0.04 per cent; the residue treated in the cold with concentrated hydrochloric acid, the solution evaporated and fused with sodium car-

[19] Die landwirtschaftlichen Versuchs-Stationen, 1890, **87** : 284.

bonate and potassium nitrate, 0.07 per cent; again, the residue treated with aqua regia to oxidize the sulfur, the solution evaporated to dryness, fused with sodium carbonate and potassium nitrate, 0.14 per cent; in all 0.25 per cent. A sample of the same soil treated directly with aqua regia, and then evaporated and fused as above, gave two-tenths per cent sulfuric acid. A sample of the same soil ignited in a crucible with sodium carbonate and potassium nitrate gave 0.16 per cent of sulfuric acid. The difference between 0.04 and 0.07 per cent can be attributed to the sulfur in the organic substance which was dissolved by the concentrated hydrochloric acid; the quantity, however, is too small to draw any safe conclusion. Possibly it might have been that the very dilute hydrochloric acid did not dissolve all of the sulfate. The quantity of sulfur combined in the organic substance in the above soil may be derived from the following equation; *viz.*,

$$\frac{0.2 - 0.07}{80} \times 32 = 0.05 \text{ per cent. of sulfur.}$$

The estimation of the sulfur in a sample of soil from Deli was carried on with still greater exactness by three different methods.

The quantities of hydrochloric acid, nitric acid, and sodium carbonate employed were measured or weighed, and the minute content of sulfuric acid therein estimated and subtracted from the final results. The methods employed were as follows:

(A) Extraction with water and afterwards with very dilute hydrochloric acid.

(B) Extraction with cold hydrochloric acid, one part to three of water.

(C) Extraction with aqua regia.

(D) Ignition with sodium carbonate and potassium nitrate.

(E) Ignition in a combustion tube with sodium carbonate in a stream of oxygen.

The percentages of sulfuric acid obtained by the different methods were as follows:

	Per cent.
(A)	0.058
(B)	0.070
(C)	0.140
(D)	0.125
(E)	0.106

431. Method of the Italian Chemists.—The determination of the sulfuric acid present as sulfates, is conducted as follows by the Italian chemists: The soil is completely extracted by diluted hydrochloric acid and the sulfuric acid precipitated in the solution with barium chlorid. If a soil is very rich in calcium sulfate it should first be treated with a warm solution of sodium carbonate to decompose the calcium sulfate, and the sulfuric acid be determined in the solution after having added hydrochloric acid.

432. Estimation of the Chlorin.—The estimation of the chlorin is of great importance in certain cases. When this element is lacking in the soil, which, however, is rare, certain plants appear to suffer from its absence. The quality of the forage plants in particular is influenced by it; but when the chlorids are too abundant, which is a frequent case, they prevent or arrest completely the progress of vegetation. Salty soils are, in general, completely sterile. In the proportion of one pound in a thousand in the earth, sodium chlorid is to be regarded as injurious. It is necessary, therefore, in analysis to take account of two cases; *viz.*, those of soils poor in chlorids and those of soils rich in chlorids.

For soils poor in chlorids the French method directs that[20] 200 grams of the earth are to be washed on a filter with boiling water. The liquor is evaporated to dryness and gently heated to a temperature inferior to redness in order to destroy the organic matter. The residue is taken up by small quantities of water and to the filtered liquor the volume of which should not exceed from 40 to 50 cubic centimeters are added ten cubic centimeters of pure nitric acid and a sufficient quantity of silver nitrate to produce a complete precipitation. The precipitate is vigorously shaken and allowed to stand for a few hours in a warm darkened locality. The precipitate is collected upon a double filter and the silver chlorid, after proper desiccation, is weighed.

When the soil is rich in chlorids it is washed as has just been described upon a filter. The wash-waters are made up to one liter and 50 cubic centimeters, equivalent to ten grams of the soil, are used for analysis. This quantity is treated exactly as described above.

[20] Annales de la Science agronomique, 8th year, 1891, 1 : 289.

rous hydroxid and the aluminum hydroxid are completely separated. Acetic acid is added in excess and until about four-fifths of the whole precipitate have passed again into solution. Then, after boiling for a moment, the whole is quickly filtered through a large filter with a cover, and the contents of the filter finally washed slightly. All the phosphoric acid is thus obtained in combination with some alumina and a very little iron. Nearly the whole of the iron and the larger part of the alumina, by this precipitation, are found in the filtrate and therefore cannot disturb the estimation of phosphoric acid in succeeding portions. The filter is filled with boiling water and a little nitric acid added and the dissolved precipitate is received in a beaker. The precipitation of the phosphoric acid is then accomplished by ammonium molybdate in the presence of nitric acid. After 24 hours all the phosphoric acid is thus precipitated and the precipitate is free from iron.

2. In the method of Schulze[14] the iron is completely, and the alumina, with the exception of a small quantity, separated, and the precipitation of the phosphoric acid is accomplished either by the addition of a small quantity of tartaric acid and afterwards magnesium sulfate, or directly when it is desired to avoid the use of tartaric acid by means of ammonium molybdate. The principle of the separation of the iron and alumina depends on the fact that when the hydrochloric acid solution is nearly neutralized with soda or ammonia, and boiled after treatment with ammonium formate, the greater part of the alumina remains in solution, while the iron and phosphoric acid are precipitated. The precipitate is quickly filtered, washed with hot water, dried, taken from the filter and fused in a silver crucible with pure caustic alkali, either soda or potash. On solution and boiling with water, the iron is completely separated from the phosphoric acid, and from the small quantity of the alumina present and the precipitation of the phosphoric acid can now be accomplished, either by saturation of the alkaline solution with hydrochloric acid and the direct addition of the magnesia solution after the addition of a

[14] Zeitschrift für analytische Chemie, 1864, **8** : 94.
Chemisches Centralblatt, 1861 : 3.

little tartaric acid and ammonia, or after the addition of nitric acid by ammonium molybdate.

In connection with this method of treatment attention is called to the fact that simple incineration of a compound containing organic phosphorus is not sufficient to secure all the phosphorus as phosphoric acid.

425. Matters Soluble in Sulfuric Acid.—It will have been noticed that of mineral acids, hydrochloric and nitric have been most frequently proposed as solvents for soil. Sulfuric acid has some advantages as a solvent, being in many respects more regular in its action and more sure in its results than those usually employed. When employed with a little mercury the organic matter contained in the sample is completely destroyed usually at the end of an hour. Moreover, the true clay (argile) is completely dissolved at the end of two hours, and any lime present is rapidly transformed into sulfate.[15] Only the silica and certain of the silicates will resist the action of the acid. Hence, by a three hours digestion of the soil at a boiling temperature all of the fertilizing elements of the sample pass into solution, while those elements unimportant as plant foods remain undissolved. The heating of the sample is begun at a low temperature, when any sulfurous acid that may arise from the reducing action of the organic matter will be given off. The heat is gradually increased with frequent shaking of the flask to avoid caking until the sulfuric acid begins to boil, usually about an hour. The boiling should be continued for three hours. In the dissolved part of the sample are found the total nitrogen, phosphoric acid, potash, soda, lime, magnesia and iron. It is better, however, to treat a second portion of the sample with acetic acid to obtain the lime and magnesia. The estimation of the dissolved constituents of the soil is conducted by any of the standard methods. This process is much like that of Goss.

426. Method of Goss.—On account of the length of time required to determine the phosphoric acid in soils by the usual methods, Goss[16] has proposed the following modification which in his hands has given satisfactory results:

[15] Aubin and Alla, Encyclopédie chimique, **4** : 174.

[16] Bulletin No. 43, Division of Chemistry : 58.

Previous to fusion the sample may be advantageously treated with hydrochloric and sulfuric acids.

To determine the titanium in the hydrochloric solution of a soil the following method as modified by Walker in the Bureau of Chemistry is used:

An aliquot part of the hydrochloric acid extract is mixed with five cubic centimeters of strong sulfuric acid and heated in a platinum dish until all hydrochloric acid is driven off and the sulfuric acid begins to decompose. After cooling, water is cautiously added to bring the volume up to about 50 cubic centimeters. The solution is then again cooled to room temperature, five cubic centimeters of three per cent hydrogen peroxid solution added, and the volume made up to 100 cubic centimeters with water. A standard solution of titanium is diluted with five per cent sulfuric acid, treated with five cubic centimeters of three per cent hydrogen peroxid, and brought to 100 cubic centimeters with five per cent sulfuric acid. The two colored solutions are allowed to stand for about three minutes and the depth of color then compared, preferably in a colorimetric camera.

Example: The hydrochloric acid extract from ten grams of soil is made up to 250 cubic centimeters. Ten cubic centimeters of this (coresponding to 0.4 gram soil) is treated as above. Five cubic centimeters of a standard solution of titanium, one cubic centimeter of which corresponds to 0.0002 gram TiO_2, are used. The colors of the two solutions are compared in nessler tubes. Fifty cubic centimeters of the colored soil solution correspond to 26 cubic centimeters of the standard. The 100 cubic centimeters then correspond to 52 cubic centimeters of the standard, which contains 0.00052 gram TiO_2.

Then, $0.4 : 0.00052 = 100 : x.$

$x = 0.13$ per cent TiO_2.

The standard titanium solution is best made from a pure solution of titanium sulfate dissolved in five per cent sulfuric acid. This stock titanium sulfate solution may be easily prepared by precipitating titanium hydrate from a solution of titanium chlorid or nitrate with ammonia, and dissolving the hydrate in sulfuric acid. The solution may be standardized by evaporating a measured volume to dryness, igniting the residue, and weighing the resulting TiO_2.

436 (bis.). Simultaneous Estimation of Different Elements.— The operations and processes for the estimation of each of the elements have been described, but it is often best to carry on an operation in such a way as to gain time by making a single decomposition upon a quantity of soil of some considerable magnitude, and using the results of the solution for the determination of the different substances. From the operations already described it will be easy to make a combination of methods by which all or nearly all the important constituents in a soil may be determined in a single sample. Of the various methods proposed, that of the committee of the French agricultural chemists may be taken as a type.[25] In the case of the estimation of lime, potash, magnesia, and sulfuric acid, in which the operation is carried on in a soil which is not incinerated, time may be saved by digesting a considerable quantity of the soil with concentrated nitric acid for a period of five hours. It is best to operate on 100 grams of the soil and increase proportionally the nitric acid. The filtrate, after washing, is made up to one liter and thoroughly shaken. From this amount of liquid, portions are used corresponding to the weights of soil upon which the operation for the determination of each of the constituents would be conducted. For example, for the estimation of lime in the case of a very calcareous earth, ten cubic centimeters representing one gram of the original sample, in the case of a soil poor in carbonates 100 cubic centimeters representing ten grams, and for the estimation of potash, magnesia, and sulfuric acid 200 cubic centimeters, representing 20 grams of the soil, should be used. This method avoids frequent weighings of the earth and separate treatments thereof by the acid.

On the other hand, in the same portion of the solution, the different elements can be estimated. For example, for the estimation of the potash as has been indicated, in the place of precipitating as a whole the sulfuric acid, lime, etc., and of afterwards separating the magnesia in the sole aim of eliminating these bodies, they can be collected separately and weighed, thus securing at a single operation several determinations.

[25] Annales de la Science agronomique, 8th year, 1891, 1 : 290.

At the beginning some barium chlorid is added and if the barium sulfate is then collected and weighed, the estimation of the sulfuric acid is effected. To the filtrate there are afterwards added some ammonia and ammonium carbonate to precipitate, at once, the excess of barium, the iron and aluminum hydroxids, the lime and the phosphoric acid. This separation being effected the filtrate contains still the magnesia and the alkalies. The first can be separated by means of oxalic acid, collected, and weighed. Finally the potash itself can be estimated in the state of perchlorate or platinochlorid. It has thus been possible in the same suite of operations to estimate in a given quantity of the liquid, the sulfuric acid, the magnesia, the lime, and the potash.

437. **Estimation of Kaolin in Soils.**—True kaolin is a hydrated aluminum silicate, having the formula $H_4Al_2Si_2O_9$. This substance is, even in concentrated hydrochloric acid, almost completely insoluble. If heated to low redness until its water of constitution is driven off it becomes soluble even in dilute acid. It contains, theoretically, 13.94 per cent of water of combination. The following methods, due to Sachsse and Becker,[26] can be used for its determination.

Estimation of the Water of Combination.—Heat from one to two grams of kaolin, dried at 100°, for half an hour in a covered platinum crucible to a temperature which shows an incipient red heat when the crucible is partly protected from the daylight with the hand. This treatment does not quite give the whole of the water of combination but nearly all of it. A kaolin is changed by this treatment into a substance which is easily soluble in dilute hydrochloric acid.

Estimation of the Kaolin in Impure Kaolins.—Mineral kaolin, or the kaolin obtained by silt analysis, is dried at 100° to constant weight. It is then treated with dilute hydrochloric acid until all matters which will pass into solution have been dissolved. The residual kaolin is then washed thoroughly with water and ignited for half an hour at a low red heat. The residual mass is a second time extracted with hydrochloric acid until the silicate no longer passes into solution. The soluble silica and alumina are then esti-

[26] Die landwirtschaftlichen Versuchs-Stationen, 1892, **40** : 245 et seq.

mated in the usual way and calculated to kaolin. The result will give the pure kaolin in the sample examined.

The estimation may also be made as follows: Two samples of the impure kaolin are dried to constant weight at 100°. One is extracted with hydrochloric acid in the manner described above and the amount of silica determined. The second is treated directly by ignition to low redness for half an hour, dissolved in hydrochloric acid and the amount of silica determined. The difference in the two percentages of silica corresponds to the silica equivalent to the pure kaolin.

Statement of Results.—It is convenient to incorporate the data obtained by the above methods with the complete mass analysis of the silicate examined. In the sample given below the analysis was made on a clay silt obtained with a velocity of two-tenths millimeter per second.

The mass analysis gave the following data:

Loss on ignition	10.04
SiO_2	51.52
Al_2O_3	17.93
Fe_2O_3	7.42
CaO	1.57
MgO	6.27
K_2O	4.1
Na_2O	1.61

The loss on ignition was made up of the combined water and a trace of humus. On gentle ignition only 7.52 per cent of water came off.

The examination of the non-ignited and the gently ignited silica by means of dilute hydrochloric acid, gave the following data:

	Non-ignited.	Gently ignited.	Difference.
Water	10.04	10.04	.....
Insoluble residue	40.	34.54	—5.46
Al_2O_3	9.04	10.	+0.96
Fe_2O_3	5.96	7.27	+1.31
SiO_2	25.27	28.	+2.73
Alkalies and alkaline earths	9.69	10.15	+0.46

By comparison of these data with those obtained by the mass analysis, the following representation of the distribution of the various components in the clay is obtained:

23.52 per cent SiO_2 in the form of quartz and undecomposed silicates:

2.93 per cent SiO_2 in the form of kaolin:

25.27 per cent in the form of easily decomposable silicates and of the hydrates of SiO_2:

7.93 per cent Al_2O_3 in the form of undecomposed silicates:

0.96 per cent Al_2O_3 in the form of kaolin:

9.04 per cent Al_2O_3 in the form of easily decomposed silicates and of hydrates:

0.15 per cent Fe_2O_3 in the form of undecomposed silicates:

1.31 per cent Fe_2O_3 in the form of kaolin:

5.96 per cent Fe_2O_3 in the form of easily decomposable silicates and hydrates:

3.55 per cent of alkalies and alkaline earths in the form of undecomposed silicates:

10.00 per cent of alkalies and alkaline earths in the form of easily decomposable silicates:

10.40 per cent of water, including a trace of humus:

Collecting these results the following statement is obtained.

The clay analyzed contained:

10.04 per cent of water, a trace of humus:

35.15 per cent of undecomposed silicates and quartz:

5.00 per cent of kaolin:

50.27 per cent of easily decomposable silicates, hydrates of SiO_2 and hydroxids. These data show an excess of 0.46 per cent over the theoretical composition of the kaolin.

ESTIMATION OF NITROGEN IN SOILS.

438. **Introductory Considerations.**—The great economic and biologic value of nitrogen as a plant food renders its estimation in soils of especial importance. It is necessary, first of all, to remember that the nitrogen present in soils may be found in four forms; *viz.*, first, in organic compounds, second, as ammonia, third, as nitric or nitrous acid, and fourth, as amido compounds. Further than this each of these classes of nitrogen may be subdivided. The organic nitrogen may be in a form easily nitrified and rendered available for plant food, or it may be inert and re-

sistant to nitrification, as in hair, or exist in an amid state. The ammoniacal nitrogen may exist in small quantities as gaseous ammonia, or be combined with mineral or organic acids. As nitric or nitrous acid the nitrogen will be found combined with bases, or perhaps in minute quantities as free acid, in passing under the influence of the nitrifying ferment from the organic to the inorganic state. To the latter state it must finally come before it is suited to absorption by plants. The amido compounds may also exist in various combinations.

In general, far the largest part of soil nitrogen, excluding the atmosphere diffused in the pores of the soil, is found in the organic state and is derived from the débris of animal and vegetable life and from added fertilizers. As ammonia, the nitrogen can only be regarded as in a transition state, arising from the processes of decay, or incomplete nitrification. As nitric acid, it is found as a completed product of nitrification, or as the result of electrical action. The processes of nitrification and the isolation and determination of the nitrifying organisms are problems intimately related to the subject of fertilizers and will be considered in the second volume of this manual. By reason of the great solubility of the nitrates, and the inability of the soil to retain them in the presence of an excess of water, there can never be a great accumulation of nitric acid in the soil save in localities deficient in rain-fall or in specially protected spots, such as caves. Moreover, there is no part of the soil which has any special power of holding back nitric acid as it passes in aqueous solution through its pores. The nitric acid, therefore, produced in the soil passes at once into growing vegetation, remains in store in dry periods, or is found eventually in the drainage waters.

Under the teachings of the earlier theories of oxidation, the formation of ammonia in soil containing much vegetable matter is thought by Berthelot and André[27] to be due to the progressive decomposition of amid principles under the influence of dilute acids or alkalies, either in the cold or at an elevated temperature or under the influence of pure water at ordinary temperatures. Soils of the above description, of themselves, contain neither free

[27] Bulletin de la Société chimique de Paris, 1891, [3], 5 : 643.

ammonia nor ammoniacal salts, and the ammonia which is found in the analysis of these soils comes from the reaction above indicated. The ammonia which is found in these soils, as well as that given off to the surrounding atmosphere, comes from the same class of decompositions, and these decompositions, in this case, are effected by the water itself, or by the alkaline carbonates of the soil. The amid principles which are thus decomposed belong either to the class of amids proper, derived by the displacement of hydrogen in ammonia by acids, or to the class of alkalamids derived from nitrogenous bases, both volatile and fixed. Among these alkalamids some are soluble in water and some insoluble, and the decomposition of these last by acids or by alkalies may furnish bodies which themselves are either soluble or insoluble in water.

To determine the nature of the nitrogenous principles in a soil rather rich in humus, Berthelot and André apply the following treatment:

A soil containing 19.1 grams of carbon and 1.67 grams of nitrogen per kilogram is first subjected to treatment, at room temperature, with a concentrated solution of potash. By this treatment 17.4 per cent of the nitrogen content is set free under the form of ammonia. One-quarter of this is obtained during the first three days; one-eighth during the next three days. Afterward the action becomes much more feeble and when continued during 40 days longer, the evolution of the gas is diminished almost proportionately to the time. It appears from the above observations that the amid principles of the soil, decomposable by potash, belong to two distinct groups, which are broken up with very unequal velocities. The soil, treated on the water-bath for 13 hours at 100° with strong potash, shows the following behavior in respect to its nitrogenous constituents: Nitrogen eliminated in the form of ammonia, 16 per cent; nitrogen remaining in the part soluble in potash, ten per cent; nitrogen remaining in the part insoluble in potash 74 per cent.

Treatment with Acid.—The insoluble nitrogenous compounds of the soil are also decomposed by dilute acids, and often more rapidly than by the alkalies. The method of treatment is substantially the same as that set forth above. The decompositions

effected either by alkalies or by acids tend in general to lower the molecular weights of the resulting products. The prolonged action of alkalies at the temperature of boiling water rendered soluble, after 26 hours of treatment, 93.6 per cent of the organic nitrogen found in the vegetable mould. By treating the earth successively with alkalies and acids 95.5 per cent of the total nitrogen were decomposed. These experiments show how the insoluble nitrogen in humic compounds can be gradually rendered assimilable. The action of vegetables is not assuredly identical with those which acids and alkalies exercise. However, both present certain degrees of comparison from the point of view of the mechanisms set in play by the earthy carbonates and carbon dioxid, as well as by the acids formed by vegetation. The reactions which take place naturally, while they are not so violent as those produced in the laboratory, make up by their duration what they lack in intensity.

For a more detailed study of the nature of the nitrogenous elements in soil the following method of treatment, due to Berthelot and André, is recommended:

Treatment of the Soil with Alkalies.—1. Reaction with cold, dilute solution of potash: Mix 50 grams of the sample, dried at 110°, with a large excess of ten per cent potash solution and place under a bell-jar containing standard sulfuric acid. The mixture is left for a long time in order to secure as fully as possible the ammonia set free.

Example: Fifty grams of a soil contained 0.0814 gram of nitrogen. Treated as above it gave the following quantities of nitrogen as ammonia:

	Nitrogen as Ammonia.
After 3 days	0.0034 gram
" 6 "	0.0054 "
" 11 "	0.0065 "
" 17 "	0.0078 "
" 25 "	0.0093 "
" 41 "	0.0107 "
" 46 "	0.0141 "

It is seen that the action still continued after 40 days. In the space of 40 days 17.4 per cent of the total nitrogen contained in

the soil had been converted into ammonia by dilute potash. According to the above observations the amid principles transformed into ammonia under the influence of dilute potash, exist in groups which are acted on with very unequal rapidity.

2. Reaction with hot dilute solution of potash: Mix 200 grams of the soil sample, with one and one-half liters of dilute potash solution containing 50 grams of potash. Place in a flask and heat on a boiling water-bath for six hours. The flask is furnished with a stopper and tubes, and a current of pure hydrogen is made to pass through the liquid, having the double object of preventing any oxidizing effect from the air and of carrying away the ammonia which may be formed. The escaping hydrogen and ammonia are passed into a bulb apparatus containing titrated sulfuric acid.

The sample of soil employed contained in 200 grams, 0.3256 gram of nitrogen. There was obtained at the end of six hours' heating, 0.0366 gram of nitrogen. In other words, 11.24 per cent of the total nitrogen in the sample appeared as ammonia.

Examination of Residue.—After the separation as ammonia as above described, pour the residue in the flask on a filter, wash with hot water, and determine nitrogen in the filtrate and in the solid matter on the filter by combustion with soda-lime. The filtrate is, of course, first evaporated to dryness after being neutralized with sulfuric acid.

The insoluble part contained 0.041 gram of nitrogen, *i. e.*, 12.84 per cent of the entire amount.

The soluble part contained 0.2411 gram of nitrogen, *i. e.*, 74.05 per cent of the whole.

Summary of Data.—In the sample analyzed the following data were obtained:

	Of the whole.
Nitrogen as ammonia	11.24 per cent.
" in insoluble part	12.84 " "
" in soluble part	74 05 " "
" not determined	1.87 " "
Sum	100.00 " "

The same experiment in which the heating on the water-bath was continued for 13 hours gave the following data:

	Of the whole.
Nitrogen as ammonia	16.02 per cent.
" in insoluble part	9.98 " "
" in soluble part	74.00 " "
Sum	100.00 " "

Further Treatment of Matter Insoluble in Hot Dilute Potash.—A portion of the insoluble portion from the last experiment is treated for 13 hours longer under the same conditions with dilute hot potash. The soluble and insoluble portions are determined as already described. Of the nitrogen insoluble after 13 hours, 64.21 per cent remained insoluble after the second 13 hours. This fact shows that a slow and progressive decomposition of the alkalamids in the soil occurs under the influence of hot dilute potash.

Treatment of Matter Insoluble in Hot Dilute Potash with Hydrochloric Acid.—A part of the material insoluble in hot potash after 13 hours is mixed with dilute hydrochloric acid, in such proportion as to have one-fifth the weight of pure hydrochloric acid to the dry solid matter. Heat in flask on a boiling water-bath for 13 hours and determine the nitrogen in the insoluble residue.

Example: In the case given it was found that 54.91 per cent of the nitrogen insoluble in dilute hot potash were dissolved by the hot hydrochloric acid.

This fact shows that insoluble nitrogen compounds contained in the soil are dissolved by dilute acids even more readily than by dilute alkalies at the temperature of boiling water.

Several reactions appear to take place simultaneously when potash is brought into contact with the nitrogenous principles of arable earth. Some of these principles, during the first period of the action become soluble and even form compounds which are not precipitable by acids. When, however, the action of the potash is prolonged, the dissolved bodies lose little by little a part of their nitrogen as ammonia or as soluble alkalamids. They become thus changed either to compounds no longer soluble in the potash, or to those insoluble in the solution when acidified. These compounds, it is true, contain nitrogen, but are poorer in this element and have a higher molecular weight, or, in other words, are condensation products. These last bodies are not absolutely stable

in the presence of potash, but are decomposed much more slowly than the original bodies from which they were derived.

In general, it may be said that under the influence of alkalies on the nitrogenous principles of the soil there is a tendency to form two classes of bodies, the one more soluble with a lower molecular weight, the other less soluble with a higher molecular weight. The inverse relation between solubility and condensation is in agreement with what is observed in similar reactions with organic bodies in general. It certainly plays an important rôle in the transformations which an arable soil undergoes, either through the mild influences of the air and natural waters, or the more energetic action of vegetables themselves.

The methods of estimating nitric nitrogen will be made the theme of a special study in connection with the chapter on nitrification in the second volume of this manual. There will be considered here, therefore, the methods of determining organic and ammoniacal nitrogen in the soil with only such incidental treatment of the methods for nitric nitrogen as the processes applicable to the other forms may contain.

439. **Earlier Methods of the Association of Official Agricultural Chemists.**[28]—The nitrogen compounds in the soil are usually placed in three classes.

1. The nitrogen combined with oxygen as nitrates, or nitrites, existing as soluble salts in the soil.

2. The nitrogen combined with hydrogen as ammonia, or organic nitrogen easily convertible into ammonia. The ammonia may exist as salts, or may be occluded by hydrated ferric or aluminum oxids and organic matter in the soil.

3. The inert nitrogen of the soil or the humus nitrogen.

Active Soil Nitrogen.—The material proposed for reducing the nitrates to ammonia, and at the same time to bring ammonia salts and organic nitrogen into a condition for separation by distillation, is sodium amalgam. Liquid sodium amalgam may be readily prepared by placing 100 cubic centimeters of mercury in a flask of half a liter capacity, covering the warmed mercury with melted paraffin, and dropping into the flask at short intervals pieces of

[28] Bulletin No. 38, Division of Chemistry : 204.

metallic sodium, the size of a large pea, taking care that the violence of the reaction does not project the contents from the flask, till 6.75 grams of sodium have combined with the mercury. The amalgam contains one-half per cent of sodium and may be preserved indefinitely under the covering of paraffin. To estimate the active soil nitrogen, place 50 grams of air-dried soil in a clean mortar, add 200 cubic centimeters of ammonia-free distilled water, rub up the soil with a part of the water to a smooth paste, transfer this to a flask of one liter capacity, washing the last traces of the soil into the flask with the rest of the water: Add 25 cubic centimeters of the liquid sodium amalgam and shake the flask so as to break the sodium amalgam into small globules distributed through the soil. Insert a stopper with a valve and set aside in a cool place for 24 hours. Pour into the flask 50 cubic centimeters of milk of lime, and distill, on a sand-bath, 100 cubic centimeters into a flask containing 20 cubic centimeters of decinormal sulfuric acid, and titrate with decinormal soda solution, using dimethyl-orange as indicator. Estimate the nitrogen of the ammonia found as active soil nitrogen.

If the ammonia produced is too small in amount to be readily estimated volumetrically, determine it by nesslerizing the distillate.

Estimation of Nitrates in the Soil.—When it is desired to estimate separately the nitrates in the soil, the following method may be used: Extract the nitrates with water, evaporate 100 cubic centimeters of the soil extract to dryness on the water-bath, dissolve the soluble portion of the residue in 100 cubic centimeters of ammonia-free distilled water, filtering out any insoluble residue, place the solution in a flask and add ten cubic centimeters of liquid sodium amalgam, insert stopper with valve, set it aside to digest in a cool place for 24 hours, add 50 cubic centimeters of milk of lime, distill and titrate as above, and estimate the nitrogen as N_2O_5.

Nesslerizing may be substituted for titration when the amount of nitrates is small.

An approximate estimation of the amount of nitrates will be of value in determining which method of estimation to use. This may be secured by evaporating a measured quantity of the soil ex-

tract, say five cubic centimeters, on a porcelain crucible cover on a steam-bath or radiator, having first dissolved a minute fragment of pure brucin sulfate in the soil extract. When dry pour over the residue concentrated sulfuric acid, free from nitrates, and observe the color reactions produced. If the nitrate (reckoned as KNO_3) left upon evaporation does not exceed the two-thousandth part of a milligram, only a pink color will be developed by adding the sulfuric acid; with the three-thousandth part of a milligram, a pink with faint reddish lines; with the four-thousandth part, a reddish color; with the five-thousandth part, a red color.

By increasing or diminishing the amount of soil extract evaporated to secure a color reaction of a certain intensity, an approximate estimate may be made of the amount of nitrates present.

Blank experiments to test the acid and the brucin sulfate will be required before confidence can be placed in such estimations.

Total Nitrogen of Soils.—The total nitrogen may be determined by combustion with soda-lime, but this process is often unsatisfactory because of the large amount of material required when the organic matter or humus is small in amount and the process has now little more than historical value.

A modification of the kjeldahl method is more easy to carry out and gives results equally satisfactory. Place 20 grams of soil in a kjeldahl flask, and add 20 cubic centimeters of sulfuric acid (free from ammonia) holding in solution one gram of salicylic acid. If the soil contain much lime or magnesia in the form of carbonate, enough more sulfuric acid must be added to secure a strongly acid condition of the contents of the flask. Add gradually two grams of zinc dust, shaking the contents of the flask to secure intimate mixture. Place the flask in a sand-bath and heat till the acid boils, and maintain the boiling for ten minutes. Add one gram of mercury and continue the boiling for one hour, adding ten cubic centimeters of sulfuric acid if the contents of the flask are likely to become solid. Cool the flask and wash out the soluble materials with 200 cubic centimeters of pure water, leaving the heavy earthy materials. Rinse the residue with 100 cubic centimeters of water, and add this to the first washings. Place this soluble acid extract in a liter digestion flask, add 35 cubic

centimeters of a solution of potassium sulfid, and shake the flask to secure intimate mixture of the contents. Introduce a few fragments of granulated zinc, pour in 75 cubic centimeters of a saturated solution of caustic soda, connect the flask with a condenser and distill 150 cubic centimeters into a flask containing 20 cubic centimeters of acid, using the same acid and alkali for titration used in the kjeldahl method under fertilizers, described in volume second.

Enter the nitrogen found in this operation as total soil nitrogen. The difference between the total soil nitrogen and the active soil nitrogen will express the inert nitrogen of the soil, that is, nitrogen as organic or amido compounds not assimilable by plants without further oxidation.

440. The Official Method.—The procedure for the determination of total soil nitrogen which is now practiced by nearly all American chemists is the official method.[29]

From seven to 14 grams of the soil, free of nitrates, are placed in a small kjeldahl digesting flask, of about 250 cc. capacity, with 30 cc. of strong sulfuric acid, or more, if necessary, and 0.7 gram of yellow oxid of mercury, and boiled for an hour. The residue is oxidized with potassium permanganate in the usual way. After cooling, the flask is half filled with water, vigorously shaken, the heavy matters allowed to subside, and the supernatant liquid poured into a flask of from 1,000 to 1,200 cubic centimeters capacity. This operation is repeated until the ammonium sulfate is practically all removed and the distillation flask is a little more than half full. The ammonia is distilled in the usual manner. When soils contain any notable quantity of nitrates or nitrites these may first be extracted with water and determined separately and the residual soil treated as above, or the modified gunning method for nitrates described in volume second of this manual be used.

441. Hilgard's Method.[30]—The humus determination will, in the case of virgin soils, usually indicate approximately the store of nitrogen in the soil, which must be gradually made available by nitrification. Ordinarily (outside of the arid regions) the deter-

[29] Bulletin No. 46, Bureau of Chemistry : 76.

[30] Bulletin No. 38, Division of Chemistry : 81.

mination of ammonia and nitrates present in the soil is of little interest for general purposes, since these factors will vary with the season and from day to day. Kedzie proposes to estimate the active soil nitrogen (ammonia plus nitrates and nitrites) by treatment of the whole soil with sodium amalgam and distillation with lime. The objection to this process is that the formation of ammonia by the reaction of the alkali and lime upon the humus amids would greatly exaggerate the active nitrogen and lead to a serious overestimate of the soil's immediate resources.

The usual content of nitrogen in black soil-humus is from six to eight per cent in the regions of summer rains. From late determinations it would seem that in the arid regions the usually small amount of humus (often less than two-tenths per cent) is materially compensated by a higher nitrogen percentage. It thus becomes necessary to determine the humus nitrogen directly; and this is easily done by substituting in the grandeau process of humus extraction potash or soda-lye for ammonia water, and determining the nitrogen by the kjeldahl method in the filtrate.

The lye used should have the strength of four per cent in the case of potassium hydroxid, and three per cent in that of sodium hydroxid. The black humus filtrate is carefully neutralized with sulfuric acid, evaporated to a small bulk in a beaker or evaporating basin, and the liquid finally evaporated to dryness in the kjeldahl flask itself by means of a current of air. The beaker or basin is washed either with some of the alkaline lye, or, after evaporation, with warm concentrated sulfuric acid, which is then used in the nitrogen determination in the usual way.

For the determination of nitrates in the soil it is, of course, usually necessary to use large amounts of material, say not less than 100 grams, and, according to circumstances, five or more times that amount. In the evaporated solution the nitric acid is best determined by the reduction method, as ammonia.

Usually the soil filtrate is clear nad contains no appreciable amount of organic matter that would interfere with the determination; yet in the case of alkaline soils (impregnated with sodium carbonate) a very dark colored solution may be obtained. In that case the soil may advantageously be mixed with a few per cent

of powdered gypsum before leaching; or the gypsum may be used in the filtrate to discolor it by the decomposition of sodium carbonate and the precipitation of calcium humate. The evaporated filtrate can then be used for the nitrate determination by either the kjeldahl, griess, or the nessler process, which will, of course, include such portions of the ammoniacal salts as may have been leached out. The above named processes will be fully described in the second volume.

For the separate determination of these and of the occluded ammonia, when desired, it is probably best to mix the wetted soil intimately with about ten per cent of magnesium oxid and distill into titrated hydrochloric acid. For general purposes, however, this determination is usually of little interest.

442. **Müller's Modified Kjeldahl Method.**—Numerous difficulties, as stated by Müller,[31] have attended the attempts to apply the kjeldahl method for the estimation of nitrogen to samples of soil, and he has modified the method to some extent and made comparisons of the quantity of nitrogen by this modified method and by the soda-lime method.

The principal difficulty encountered by him has been in the regular heating of the mixture of fuming sulfuric acid and soil. The particles of soil are deposited at the bottom of the flask and the result is that the bottom layers become overheated, and, being poor conductors of heat, fail to transmit a sufficient quantity of heat to penetrate to the upper layers of the liquid to complete the reaction. In order to avoid this difficulty Müller heats his flask in a small stove formed with a straight vertical cylinder of iron or copper, the upper end of which is covered with a sheet of iron pierced with a hole which allows the neck of the flask to pass through, while the lower end is closed with a piece of sheet iron furnished on its upper surface with a layer of asbestos. This cylinder of metal is surrounded with a second one, concentric with the first, through which passes a current of heated gases furnished by an ordinary bunsen. By heating the flask in this stove or furnace an even distribution of the heat is secured to all parts of the mixture, but the little drops of sulfuric acid, which are condensed

[31] Annales de Chimie et de Physique, 1891, [6], **22** : 393.

on the cold part of the neck, sometimes lead to the fracture of the glass as they run down the sides of the flask to the hot portions. To prevent the reflux of this condensed acid, which only needs to be done near the end of the reaction, when it is necessary to heat to a very high temperature, the neck of the flask is bent at the point immediately above its emergence at the upper surface of the furnace, so as to dip slightly towards its mouth, and carried into a flask of about 75 cubic centimeters capacity, which will receive the drops of sulfuric acid condensed during the operation. The furnace has the following dimensions; height, 12 centimeters; diameter of interior cylinder, five and one-half centimeters; diameter of exterior cylinder, seven and one-half centimeters.

It is supported on a triangle of large iron wire and is heated by an ordinary bunsen, or by a concentric bunsen, according to the temperature which it is necessary to obtain. The proportions which should be observed between the amount of earth employed and the sulfuric acid are about as follows:

Of the dry earth, 15 grams; of the fuming sulfuric acid, 30 cubic centimeters. There should also be added to the mixture about three-tenths of a gram of pure stearic acid, or better, benzoic acid to aid in converting the organic nitrogen into ammonium sulfate. When the soil to be analyzed does not contain carbonate, the sulfuric acid should be added in two portions. At first add about 20 cubic centimeters of the acid, and after shaking it, the other ten cubic centimeters, running it in from a burette or a pipette in such a manner as to wash thoroughly the neck and sides of the flask. If the earth contain carbonate, however, it is necessary to add the fuming acid in small portions of about five cubic centimeters at a time, waiting each time until the disengagement of the gas caused by the previous addition has ceased. A soil which contains from 30 to 40 per cent of calcium carbonate should be carefully treated in a porcelain capsule with a slight excess of sulfuric acid, pure and dilute. The mixture is afterwards to be evaporated to dryness upon a sand-bath and the residue heated in a drying oven to 110°. The mass is then pulverized, introduced into the flask, treated with three-tenths of a gram of benzoic acid and 30 cubic centimeters of fuming sulfuric acid,

and heated as indicated above. In all cases it is necessary to continue the heating until the contents of the flask are colorless.

With soils containing considerable quantities of iron, howevr, a slight red color will probably be observed which will not interfere with the accuracy of the tests.

The heating should at first be gentle and the temperature afterward elevated little by little, and finally the heat should be sufficiently great to distill about one and one-half cubic centimeters of sulfuric acid. The operation lasts from 12 to 18 hours. When the reaction is terminated, the cooled mass is taken up with water absolutely free from ammonia, filtered into a flask, and washed upon the filter until the volume of the filtered liquid is about 350 cubic centimeters. Afterward an excess of soda-lye, at 50° Baumé is added, a few pieces of quartz to facilitate boiling, the flask connected with a condenser, the liquid distilled and received in a conical flask closed by a cork having two holes, one of which permits the entrance of the end of the condenser, and the other of a glass tube which is connected with a small flask containing water, the neck of the receiving flask being inclined toward the condenser to avoid the entrainment of any of the alkaline liquid which may be distilled. The distilling flask rests upon two or three pieces of sheet iron, is heated with an ordinary burner, and the ebullition is perfectly regular. From 170 to 180 cubic centimeters of the liquid are distilled in from three and one-half to four hours. The distilled liquid, treated with a few drops of litmus, is titrated by a solution of sulfuric or hydrochloric acid, of which one cubic centimeter corresponds to 0.001 cubic centimeter of nitrogen. The operation both in digestion and distillation appears to be excessively prolonged.

443. **Modification of the Kjeldahl Method by Arnold and Wedemeyer.**[32]—For the oxidizing liquid, a mixture of three grams of benzoic acid with 40 cubic centimeters of H_2SO_4 is employed. After placing the mixture in the digestion flask with the sample of soil, the whole is gently shaken for a few minutes to prevent clotting. The temperature is then raised until acid vapors begin to come off, when one gram of copper sulfate and one gram of

[32] Zeitschrift für analytische Chemie, 1892, **31** : 525.

mercuric oxid are added; and after from ten to 15 minutes to avoid foaming, from ten to 20 grams of potassium sulfate are added. The sublimate noticed on the walls of the flask is benzoic acid and does not interfere with the accuracy of the determination.

This method has given good results with the alkaline nitrates, the nitrates of barium, mercury, silver, lead, and with strychnia, ammonia, pyridin, azobenzol, dinitrobenzol, and picric acid.

444. Prevention of Bumping During Distillation.—Daffert has employed the modified kjeldahl method, but found considerable difficulty owing to the violent bumping of the liquid in the distillation. This was especially the case where the sample contained a large proportion of sand. To overcome this annoyance and danger he devised the following process:[33]

Fit into the mouth of a large-mouth distillation flask a stopper having two perforations. Through one of the perforations pass the usual distillation tube, through the other a similar tube connected with a supply of steam. Bring the contents to a brisk boil, after which a small current of steam is turned on, and passed in a small stream through the contents of the flask during the distillation. By this means, not only is all danger from bumping avoided, but the time required for the distillation shortened. By the old method it usually requires from 15 to 20 minutes, whereas when the above device is used the distillation requires only from six to ten minutes.

445. Determination of Organic Nitrogen by the Soda-Lime Method.—In the description of the method following, the directions of the French Committee of Agricultural Chemists have been made the base of the analytical process.[34] This method is, in this country, almost superseded by the moist combustion process with sulfuric acid. By reason of its long use, however, and because it has been employed by the agricultural chemists of France, Italy, and England, in numerous recorded data, it merits a full description. It is recommended also by Berthelot and

[33] Relatorio annual do Instituto agronomico do Estado São Paulo, (Brazil), 1893, Article XIV : 107.

[34] Annales de la Science agronomique, 8th Year, 1 : 253, et seq.

André,[35] by the International Congress of Chemists, held in Paris in 1889, by the Italian chemists, and by the official Belgian method,[36] in all cases where nitrates are not present in notable quantities. It is only fair to say, however, that these recommendations were made before the kjeldahl process was generally introduced. The nitrogen determinations made in the Division of Chemistry were also conducted by this method for many years before the modern methods of procedure were introduced.

The nitrogen which is found in soils in the organic state is transformed into ammonia when it is heated with soda-lime. This reaction is the base of the process of analysis which has so long been used for this class of bodies. The analytical process is conducted as follows:

A well-cleaned glass combustion tube, closed at one end, is used. The length of the tube is from 35 to 40 centimeters. It is filled first to a depth of two centimeters with calcium oxalate; afterwards to a depth of five centimeters with soda-lime in small fragments; then with the mixture to be analyzed; *viz.*, ten grams of the sample of soil, or 20 grams if poor in nitrogen and organic matters, mixed with soda-lime reduced to a coarse powder. This mixture should occupy a length of about 20 centimeters in the tube. The soil and soda-lime are mixed in a mortar. Afterwards the mortar is rubbed with small quantities of soda-lime, and this, together with the copper boat which has been used in introducing the mixture, is thoroughly washed with the soda-lime, which is poured into the tube until it is filled to within four centimeters of its open extremity. The open end of the tube is closed with a wad of asbestos packed sufficiently tight to prevent the carrying off of the soda-lime by the gas which may be generated during the combustion. The combustion is commenced by heating the tube near the open extremity until it is red and carrying the heat progressively towards the part containing the soil mixed with the soda-lime. An ordinary gas combustion furnace is used and the heat graduated in such a way that the bubbles of gas pass off regularly and not too rapidly. The gas is conducted into

[35] Annales de Chimie et de Physique, 1892, [6], **25** : 300.

[36] Petermann, L'Analyse du Sol, Brussels, 1891 : 17.

a bulb tube containing a decinormal standard sulfuric acid colored with litmus. The combustion is continued until the whole of the organic material is decomposed, care being taken not to raise the combustion tube above a low redness in order to avoid its softening. At the end, however, the temperature of the combustion tube is raised to a bright red, and the part containing the calcium oxalate is heated little by little for the purpose of evolving hydrogen, which is used to drive out the last traces of ammonia. After the combustion is completed, and the last traces of ammonia driven out, the standard acid which has received the evolved ammonia is removed, the tube leading to it washed, the wash-water collected with the rest of the liquid and titrated with a standard solution of lime-water, the strength of which has previously been determined against standard sulfuric acid.

446. **Preparation of the Standard Sulfuric Acid.**—The sulfuric acid to be used in making the standard solutions is previously boiled for half an hour in a platinum dish and allowed to cool in a desiccator. The solution contains 61.25 grams of sulfuric acid in one liter. It is recommended that the flask which holds the sulfuric acid be one which has been used for a long time for holding concentrated sulfuric acid, in order to forestall any action of the alkali in the glass upon the acid after its strength has been determined. The solution before described is of such strength as to have each cubic centimeter equivalent to one milligram of nitrogen.

For the estimation of the nitrogen in the soil a tenth normal solution is used, which is prepared by taking 100 cubic centimeters of the normal solution, described above, and diluting to one liter.

Preparation of the Lime-Water.—From 200 to 300 grams of slaked lime are placed in a closed flask of about five liters capacity. This is filled with water and shaken frequently, and left to deposit the matter in suspension. The water which contains the saline particles which may have been present in the lime is poured off. Fresh water is poured on and the flask shaken from time to time. To use this lime-water the clear part of it is decanted into a flask, avoiding, as much as possible, access to the air. The flask

is closed with a cork carrying two tubes drawn out and bent at a right angle. One of these serves for pouring off the water and the other serves for the entrance of the air, which should be free of carbon dioxid. These two tubes are themselves closed by means of a rubber tube carrying a pinch-cock. The strength of the lime-water is fixed by titration with the decinormal standard sulfuric acid.

Preparation of the Soda-Lime.—Six hundred grams of slaked lime in fine powder are saturated with 300 grams of caustic soda dissolved in 300 cubic centimeters of water. The whole is rubbed into a paste and introduced into a crucible which is heated to redness. The contents of the crucible, still hot, are poured out. and rapidly reduced to fragments in a copper mortar in such a manner as to have the pieces about the size of a pea, and without having too much finely powdered soda-lime mixed with them. While still hot it is placed in a flask and well-stoppered. In order that this reagent should contain no nitrogen it is indispensable to use in its preparation materials which contain no trace of nitrates.

Preparation of the Calcium Oxalate.—In a small copper vessel place 100 grams of oxalic acid and add gradually, bringing it to boiling, enough water to dissolve it. Afterwards place in the solution small portions of slaked lime in a state of powder, constantly testing it until turmeric paper indicates that there is a little lime in excess. It is then evaporated, stirring vigorously on the open fire, and the evaporation is finally finished on a steam-bath. The dried material is placed in a flask and well-stoppered. The oxalic acid which is used in this preparation should be free from every trace of nitrogen.

Preparation of the Litmus Solution.—Five grams of litmus are placed in a flask with a flat bottom. Afterwards a few cubic centimeters of ammonia are added, 25 grams of crystallized sodium carbonate, and ten cubic centimeters of water. This mixture is left to digest for some time, with frequent stirring, at a temperature of from 60° to 80°. The digestion is finished in about four or five days, during which time, at intervals, a few drops of ammonia are added, sufficient to maintain always the ammoniacal odor. At the end of this time 200 cubic centimeters of water are

added and the digestion allowed to continue several days more, still maintaining the solution alkaline with ammonia. A slight excess of hydrochloric acid is added, and the matter which is precipitated is received upon a filter where it is washed several times with cold water and allowed to dry at a low temperature.

For use, from one to two grams of this dry precipitate are dissolved in 100 cubic centimeters of alcohol, and there is thus obtained a litmus solution of extreme sensibility.

447. **Treatment of Soil Containing Nitrates.**—Nitrates exist in small quantities in all arable soils, except perhaps after prolonged and heavy rains. When treated for nitrogen by the soda-lime method above described, a part of the nitric nitrogen is changed to the state of ammonia, while another part escapes estimation altogether, causing an error in case of soils having much nitrate, which it is important to consider. When the soils contain only small quantities of nitrates, this error is insignificant and does not affect sensibly the results, but in the case of earths rich in nitrates it is necessary first to eliminate them before the determination of the nitrogen by the soda-lime method. The operation is carried on as follows:

Twenty grams of the soil are washed on a small funnel, furnished with a plug of asbestos, with small quantities of pure water, in such a way as to cause from 30 to 40 cubic centimeters of water to pass through. The whole of the nitrate is thus removed. The soil is dried and submitted to analysis by the soda-lime method as just described. There are removed with the nitrate only small traces of organic nitrogen, too small to influence the results of the analysis. If, however, it is desired to remove altogether this slight cause of error, evaporate the wash-waters, above described, to two or three cubic centimeters; add a few drops of concentrated solution of ferrous chlorid and as much hydrochloric acid, and boil some minutes in order to drive off, in the state of nitrogen dioxid, all the nitric acid. The residue is evaporated to dryness and contains the traces of organic nitrogen. This is added to the soil which is to be treated by the soda-lime method.

448. Müller's Method.—The determination of nitrogen in the soil by soda-lime is carried on as follows by Müller:[87]

Fifteen grams of fine earth, dried and mixed with a little sugar, are mixed with 30 grams of soda-lime in powder. The bottom of the combustion tube contains a little moist soda-lime, which is heated at the end of the operation at the same time that a current of pure hydrogen is made to pass through it, and the temperature of the tube is raised, little by little, to a distinct redness. The contents of the receiving bulbs are distilled, after the addition of water and soda, in the same apparatus which served in the estimation of nitrogen, by the kjeldahl method, as described in paragraph **442**, the determinations and titrations are made also under the same conditions.

Blank determinations are also made under the same conditions to determine the amount of correction to be made by the two methods. In one case soda-lime, heated with pure sugar, gave 0.0002 gram of nitrogen for a total weight of 55 grams of the soda-lime contained in the tube. The fuming sulfuric acid gave 0.0011 cubic centimeters of ammoniacal nitrogen for the volume of 30 cubic centimeters.

The numbers obtained by the kjeldahl method in general, are lower than those obtained by the soda-lime method when no stearic or benzoic acid is used. The numbers obtained when stearic acid alone was used were sometimes inferior to those obtained by the soda-lime method.

The numbers obtained when benzoic acid is used are, in general, about the same as those obtained by the soda-lime method.

It would seem that the double distillation, outlined above, for the kjeldahl method, would not be required if due care were exercised in the first distillation. This variation, therefore, seems to be unnecessary.

In the soda-lime method, time would be saved by the reception of the ammonia in standard acid, and its titration in the usual way, unless a further purification of the nitrogenous products of the combustion by the final distillation be desired.

[87] Annales de Chimie et de Physique, 1891, [6], **22** : 398.

449. Volumetric Determination of the Nitrogen.—Instead of separating the nitrates, the total nitrogen in the soil can be determined directly by the classic method of Dumas, which consists in bringing the whole of the nitrogen into a gaseous state and afterwards measuring its volume.

The following method illustrates the general principles of the determination:

A glass combustion tube closed at one end, about one meter in length, is selected. In the bottom of this tube is placed some potassium bicarbonate in a crystalline form, in small pieces, filling the tube to a distance of about 20 centimeters. Afterwards copper oxid is placed to the depth of ten centimeters and finally a mixture of from 20 to 30 grams of the earth with from 30 to 40 grams of copper oxid in a fine state of subdivision, and about ten grams of metallic copper obtained by reducing the copper oxid by hydrogen. Next the tube is filled with copper oxid to a depth of from 20 to 25 centimeters, and afterwards with reduced copper to the depth of at least 25 centimeters, and after this another layer of copper oxid of about five centimeters, and finally a plug of asbestos. The combustion tube is closed with a stopper carrying a glass tube of about 90 centimeters in length, of which the extremity, bent into the form of a **U**, extends to a mercury trough. The glass combustion tube is surrounded with brass gauze, except that part which contains the potassium bicarbonate. The beginning of the operation consists in heating the tube to decompose a part of the potassium bicarbonate, until the whole of the apparatus is filled with carbon dioxid. In order to determine that the whole of the air has been expelled and that the apparatus is entirely filled with carbon dioxid, a part of the gas which is disengaged, is received into a jar filled with mercury, in which a little potash-lye has been placed. If the gas is entirely absorbed by the potash, so that there remain only unappreciable particles, the tube can be regarded as completely free of air. When assurance is given that the air is all out of the apparatus, a jar of about 300 cubic centimeters capacity, filled with mercury and containing from 30 to 40 cubic centimeters of a solution of potash of a density of 42° Baumé, is placed over the outlet tube. The combus-

tion is commenced by heating the anterior part of the tube, avoiding the heating of the part containing the earth. When the first part of the tube has reached the red stage the part containing the earth is gradually heated in order to obtain a gentle evolution of gas. The temperature of the tube is carried to redness and the heating gradually carried back toward the closed extremity, but avoiding raising the temperature of the part containing the potassium bicarbonate. The red heat is continued as long as bubbles of gas are discharged into the reservoir. When the evolution of gas has ceased the apparatus is again filled with carbon dioxid for the purpose of driving out the last traces of nitrogen, by heating again the part of the tube containing the potassium bicarbonate. The evolution of the carbon dioxid should be maintained for about 15 minutes. At the end of this time all the nitrogen will be found in the receiving jar. Sometimes a small quantity of nitrogen dioxid is formed incidentally in the operation. After waiting for a quarter of an hour, in order to permit all the carbon dioxid which may have escaped into the reservoir to be completely absorbed, the receiving jar is carried to a water-basin and the mercury allowed gradually to escape; its place being taken by the water. The gas is then transferred into an azotometer where its volume and temperature are read in the usual way.

In order to absorb any nitrogen dioxid which may be admixed with the nitrogen itself, a little crystal of ferrous sulfate is introduced. The reservoir containing the nitrogen is carried to the mercury trough, and the water which it contains is nearly all run out in such a way as to be replaced with mercury, great care being exercised to avoid any escape of gas. Afterwards there is introduced over the mercury a crystal of ferrous sulfate and the azotometer is shaken until this crystal is dissolved by the water which it still contains. It is then allowed to remain for 20 hours. At the end of this time the nitrogen dioxid is absorbed and the volume of the gas is again read as before. One-half only of the total loss should be subtracted, since the volume of the nitrogen dioxid is twice the volume of the nitrogen itself. For the practice of this method, in connection with the use of a mercury pump, the directions which will be given under fertilizers in volume second, may be consulted.

450. Estimation of Ammonia.—Ammonia exists ordinarily only in very small quantities in the soil, since it is incessantly transformed into nitrate or diffused in the air. Nevertheless, it is sometimes interesting to determine its quantity. It is rarely found in a free state, but in combination with carbonic acid the humic acids or other free acids in the soil.

The method of determining the ammonia in soils is one of extreme delicacy on account of the small proportion therein, and the difficulty of expelling it without at the same time converting some of the organic nitrogen into ammoniacal compounds. The various methods employed for this purpose may be classified as follows:

1. Treatment of the soil with soda-lye in the cold, and the absorption of the ammonia given off by standard sulfuric acid.

2. The method of Boussingault, which consists in replacing the soda-lye with magnesia and distilling the ammonia at a boiling temperature, absorbing the distillate in a standard acid.

3. A modification of the above method, due to Schlösing, which consists first in extracting the ammonia by hydrochloric acid and subjecting the extract to distillation with magnesia.

4. The method of Knop consists in treating the soil in a closed cylinder with soda-lye containing bromin. The ammonia set free by the lye is decomposed in the presence of bromin into free nitrogen and hydrobromic acid. The nitrogen is collected and measured in an azotometer. The brom-soda-lye is prepared by dissolving 100 grams of sodium hydroxid in 1,200 cubic centimeters of water and adding 25 cubic centimeters of bromin.

5. The process described under 4, as shown by Baumann,[38] does not give accurate results and it has been modified by him as follows: Two hundred grams of soil are treated with 100 cubic centimeters of dilute hydrochloric acid (one part acid and four of water) free of ammonia; 300 cubic centimeters of ammonia-free distilled water are added and digested for two hours with frequent stirring. If a soil contain much calcium carbonate larger quantities of acid must be used. Two hundred cubic centimeters of the filtrate are placed in an evolution flask, connected with an

[38] Die landwirtschaftlichen Versuchs-Stationen, 1886, **33** : 247 et seq.

azotometer, with five grams of freshly burned magnesia. The flask is fitted with a stopper carrying two glass tubes, one of which reaches to the bottom and serves to introduce the ozone. The mixture is then oxidized as follows: Ozone is generated by adding three parts by weight of sulfuric acid to one part of dry and powdered potassium permanganate. A stream of air is drawn through the ozone generator by an aspirator, and the ozone is conducted into the flask containing the hydrochloric acid extract of the soil and magnesia. The oxidation is completed in about ten minutes. The mixture is then brought into the azotometer and the nitrogen set free and measured in the usual way.

It has been shown that if asparagin or glutamin be present in the soil they are decomposed by the soda-lye and the results obtained are too high. It has been further proved that soils which contain a notable quantity of humus give, with soda-lye in the cold, a practically continuous evolution of ammonia. Moreover, soils which are rich in humus and which have been treated by distillation with magnesia give, on subsequent treatment with soda-lye, considerable additional quantities of ammonia.

Comparison of Methods of Estimating Ammonia.—Baumann has determined the ammonia-nitrogen in various soils by the soda-lime method, distillation of the hydrochloric acid extract with magnesia, and the azotometric method modified as indicated above. These methods will be designated as 1, 2, 3, respectively in the following table.

	Method.		
	1.	2.	3.
	Ammonia-nitrogen in one kilogram of soil.		
No. of sample.	Gram.	Gram.	Gram.
1	0.0448	0.02227	0.02781
2	0.0168	0.01105	0.01326
3	0.0336	0.01771	0.02212
4	0.0056	0.00443	0.00443
5	0.0280	0.02337	0.02894
6	0.0196	0.01243	0.01672

From the above figures it is seen that the method usually attributed to Schlösing gives uniformly higher numbers than either of the other processes, while the third gives slightly higher values than the second.

451. The Magnesia Distillation Process.—If a sample of soil be

distilled directly with magnesia and water, there is danger on the one side of not extracting all the ammonia, by reason of the absorbing power of these bodies, and on the other, of transforming into ammonia the nitrogen of the oragnic matters. It is therefore preferable to separate the ammonia from the soil in the form of chlorid, and to subject this extract to distillation.

In a small sample of the soil the humidity is determined by drying at 100° until there is no further loss of weight. The quantity of moisture being known, 200 grams of air-dry soil are moistened with water, and then there is added, in small portions, some dilute hydrochloric acid, shaking frequently until the whole of the calcium carbonate present is decomposed. The liquor should remain acid at the end of the operation, but without containing a notable excess of acidity. Knowing beforehand the quantity of moisture contained in the 200 grams, water is added until the total quantity shall be equal to 500 cubic centimeters. The whole is then shaken and allowed to repose, filtered rapidly, covering the funnel with a glass vessel and receiving the liquid which runs through in a flask with a narrow opening. Two hundred and fifty cubic centimeters of this liquor, or mixture, represent 100 grams of earth of known humidity. This quantity is introduced into a flask for determining the ammonia and five grams of calcined magnesia added. Before commencing the distillation, assurance should be had that the magnesia has completely saturated the acid in excess, and that the liquor is alkaline.

If, by chance, the liquor should be still acid it would be necessary to add sufficient magnesia in order that the reaction should be manifestly alkaline. Afterwards the distillation is begun and the ammonia is received in an appropriate vessel containing one-tenth normal sulfuric acid and titrated in the usual way, or, if in minute quantity, nesslerized.

Inasmuch as the quantities of ammonia contained in the soil are generally very small it is necessary to be very particular in order to avoid errors. The distilled water which is employed should be deprived of all traces of ammonia by prolonged ebullition, and the hydrochloric acid should be distilled in the presence of a little sulfuric acid. The treatment with hydrochloric acid is for the

purpose of destroying the absorbing properties of the soil for ammonia, and to permit this last to enter into solution as chlorid. When there is need of very great precision it is convenient to make a blank operation with the hydrochloric acid and water which are employed, in order to make a correction for the traces of ammonia which these reagents may contain.

452. Estimation of Ammoniacal and Amid Nitrogen by the Method of Berthelot and André.[39]—Heat 100 grams of earth for 13 hours on a steam-bath with about 500 cubic centimeters of dilute hydrochloric acid (15 grams of hydrochloric acid to 500 cubic centimeters of water). At the end of this time throw the contents of the flask on a filter and wash with hot water until the acid reaction has ceased. Determine both the ammoniacal and amid nitrogen in the soluble, and the total nitrogen in the insoluble portion, the ammoniacal by distillation with magnesia, and the amid and total with soda-lime.

Example. A soil contained 0.1669 per cent total nitrogen. Of this there were obtained:

	Per cent.
As ammoniacal nitrogen	13.7
In the soluble part as amid nitrogen	56.2
In the insoluble part, total nitrogen	29.7
Sum	99.6

Treatment of the Insoluble Portion.—Treat the part insoluble in hydrochloric acid with a three per cent solution of potash on a steam-bath for 13 hours. Estimate the nitrogen remaining insoluble, from which the part dissolved can be determined by difference. The potash will dissolve usually about two-thirds of the remaining nitrogen.

About 90 per cent of the total nitrogen present in an arable soil will be rendered soluble by successive treatment with acid and alkali. The reverse treatment will give practically the same result. It is therefore immaterial, from an analytical standpoint, whether the acid or alkali be used first.

453. Estimation of Volatile Nitrogenous Compounds Emitted by Arable Soil.—The following method, due to Berthelot and André,[40] may be practiced:

[39] Annales de Chimie et de Physique, 1892, [6], **25** : 327.

[40] Annales de Chimie et de Physique, 1892, [6], **25** : 330.

Porcelain pots, containing one kilogram of soil, are placed under bell-jars of 50 liters capacity adjusted to glass dishes designed to receive the waters of condensation.

During the first period the pots are to be sprinkled from time to time, during the duration of the experiment, through the upper tubulature, so as to prevent the soil from becoming dry. The evaporated water is partly condensed on the sides of the bell-jar. It is removed each week through the inferior tubulature, treated with a little dilute sulfuric acid, and preserved for further study. A small vessel containing dilute sulfuric acid is placed under the bell-jar near the porcelain pot for the purpose of collecting, as far as possible, the evolved ammonia.

During the second period the pots are not sprinkled, the soil becomes dry and there is no longer any condensation of water on the walls of the bell-jar. The two periods should include about five months, from May to October.

At the end of the second period the following determinations are to be made:

1. The ammonia absorbed by the dilute sulfuric acid.

2. The ammonia set free by distillation with magnesia, such as may have accumulated in the condensed water.

3. The organic nitrogen contained in the latter after elimination of the ammonia. This is determined by adding a slight excess of acid, evaporation to dryness, and combustion with soda-lime, or by moist combustion with sulfuric acid.

Example:

Earth Employed.—One kilogram of sandy clay containing total nitrogen, 0.09 gram. Nitrogen in sprinkling water, 0.000048 gram.

Nitrogen in Exhaled Products:—

FIRST PERIOD. SPRINKLING.

	Gram.
Ammoniacal nitrogen collected in the dilute sulfuric acid	0.00012
Ammoniacal nitrogen collected in the condensation waters	0.00012
Organic nitrogen in condensation waters	0.00220
Sum	0.00244

SECOND PERIOD. NO SPRINKLING.

Ammoniacal nitrogen in dilute sulfuric acid	0.000007
" " " condensed water	0.000007
Organic " " " "	0.000040
Sum	0.000054

Conclusions.—The exhalation of nitrogenous compounds takes place with a certain relative activity, about two milligrams in two months and a half, as long as the soil is kept moist by sprinkling.

In the second period, without sprinkling, the exhalation is reduced to a mere trace.

The vessel containing the dilute sulfuric acid placed near the porcelain pot absorbs only about one-half of the ammoniacal nitrogen set free. The nitrogen emitted under other forms than ammonia is, in every instance, greatly superior in quantity, and this is the most important of the observed phenomena. This is true at least with the kind of soil with which the experiment was made. With arable soil containing 20 times as much nitrogen as the soil described above this order is reversed,[41] the ammoniacal prevailing over the non-ammoniacal nitrogen volatilized.

These phenomena are doubtless greatly influenced in soil under culture by microbes, and the lowest orders of vegetation to which are doubtless due the traces of non-ammoniacal volatile nitrogenous compounds, a sort of vegetable ptomaines.

454. General Conclusions.—In the light of our present knowledge concerning the methods of nitrogen determination in the soil in the form of organic compounds and ammonia, moist combustion with sulfuric acid is to be preferred to the older methods. For the nitrogen combined as ammonia, the extraction of the sample with hydrochloric acid and subsequent distillation with an excess of freshly calcined magnesia, are recommended. For the study of the progressive decomposition of the nitrogenous compounds, the various processes devised by Berthelot and André are the best.

The origin of the nitric acid in the soil, the methods of studying the various nitrifying organisms, and of estimating the nitric acid produced, will form the subject of part seventh and be further considered in the second volume.

[41] Annales de Chimie et de Physique, 1890, [6], **19** : 492.

added and the digestion allowed to continue several days more, still maintaining the solution alkaline with ammonia. A slight excess of hydrochloric acid is added, and the matter which is precipitated is received upon a filter where it is washed several times with cold water and allowed to dry at a low temperature.

For use, from one to two grams of this dry precipitate are dissolved in 100 cubic centimeters of alcohol, and there is thus obtained a litmus solution of extreme sensibility.

447. **Treatment of Soil Containing Nitrates.**—Nitrates exist in small quantities in all arable soils, except perhaps after prolonged and heavy rains. When treated for nitrogen by the soda-lime method above described, a part of the nitric nitrogen is changed to the state of ammonia, while another part escapes estimation altogether, causing an error in case of soils having much nitrate, which it is important to consider. When the soils contain only small quantities of nitrates, this error is insignificant and does not affect sensibly the results, but in the case of earths rich in nitrates it is necessary first to eliminate them before the determination of the nitrogen by the soda-lime method. The operation is carried on as follows:

Twenty grams of the soil are washed on a small funnel, furnished with a plug of asbestos, with small quantities of pure water, in such a way as to cause from 30 to 40 cubic centimeters of water to pass through. The whole of the nitrate is thus removed. The soil is dried and submitted to analysis by the soda-lime method as just described. There are removed with the nitrate only small traces of organic nitrogen, too small to influence the results of the analysis. If, however, it is desired to remove altogether this slight cause of error, evaporate the wash-waters, above described, to two or three cubic centimeters; add a few drops of concentrated solution of ferrous chlorid and as much hydrochloric acid, and boil some minutes in order to drive off, in the state of nitrogen dioxid, all the nitric acid. The residue is evaporated to dryness and contains the traces of organic nitrogen. This is added to the soil which is to be treated by the soda-lime method.

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Blank determinations are also made under the same conditions to determine the amount of correction to be made by the two methods. In one case soda-lime, heated with pure sugar, gave 0.0002 gram of nitrogen for a total weight of 55 grams of the soda-lime contained in the tube. The fuming sulfuric acid gave 0.0011 cubic centimeters of ammoniacal nitrogen for the volume of 30 cubic centimeters.

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tion is commenced by heating the anterior part of the tube, avoiding the heating of the part containing the earth. When the first part of the tube has reached the red stage the part containing the earth is gradually heated in order to obtain a gentle evolution of gas. The temperature of the tube is carried to redness and the heating gradually carried back toward the closed extremity, but avoiding raising the temperature of the part containing the potassium bicarbonate. The red heat is continued as long as bubbles of gas are discharged into the reservoir. When the evolution of gas has ceased the apparatus is again filled with carbon dioxid for the purpose of driving out the last traces of nitrogen, by heating again the part of the tube containing the potassium bicarbonate. The evolution of the carbon dioxid should be maintained for about 15 minutes. At the end of this time all the nitrogen will be found in the receiving jar. Sometimes a small quantity of nitrogen dioxid is formed incidentally in the operation. After waiting for a quarter of an hour, in order to permit all the carbon dioxid which may have escaped into the reservoir to be completely absorbed, the receiving jar is carried to a water-basin and the mercury allowed gradually to escape; its place being taken by the water. The gas is then transferred into an azotometer where its volume and temperature are read in the usual way.

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bromin escapes the beaker is allowed to cool somewhat, more ammonia and bromin water being added and heated as before. This process is continued until the manganese is completely precipitated, which requires from 15 to 30 minutes. The solution is then to be slightly acidified with a few drops of acetic acid and filtered while still boiling hot, the precipitate washed with hot water, dried, ignited, and weighed as Mn_3O_4.

(d) *Determination of Calcium.*—If no manganese be precipitated, evaporate solution B or the filtrates and washings from (c) to about 50 cubic centimeters, make slightly alkalinity with ammonia, and add, while still hot, ammonium oxalate solution so long as any precipitate is produced, adding a few cubic centimeters in excess to convert the magnesium also into oxalate. Heat to boiling, allow from 15 to 20 cubic centimeters of hot distilled water on the precipitate, and again decant the clear solution on the filter. Dissolve the precipitate in the beaker with a few drops of hydrochloric acid, add a little water, and reprecipitate, boiling hot, by adding ammonium hydroxid to slight alkalinity and a little ammonium oxalate solution; filter through the same filter, transfer the precipitate to the filter, and wash it free from chlorids; dry, ignite the precipitate over the blast lamp until it ceases to lose weight, weigh, and estimate as CaO.

(e) *Determination of Magnesium.*—Slightly acidify the filtrate and washings from (d) with hydrochloric acid and concentrate to about 50 cubic centimeters, place in a small erlenmeyer flask or beaker, make slightly alkaline with ammonium hydroxid, and add sufficient acid sodium phosphate solution to precipitate the magnesium; then add gradually ten cubic centimeters of strong ammonium hydroxid, cover closely to prevent escape of ammonium, and let stand in the cold. Filter after 12 hours, wash the precipitate free from chlorids, dry, burn at first at a moderate heat, finally igniting intensely, and weigh as $Mg_2P_2O_7$.

(f) *Determination of Ferric Oxid.*—Evaporate 100 cc. of solution A, with the addition of about ten cubic centimeters of sulfuric acid, until all hydrochloric acid is expelled; dilute with water, reduce with zinc, and estimate iron oxid by a stand-

ard solution of potassium permanganate. To prepare potassium permanganate solution, dissolve 3.156 grams of the pure salt in 2,000 cubic centimeters of distilled water, and preserve in a glass-stoppered bottle, shielded from the light. Standardize this solution after it has stood 24 hours with pure ammonia-ferrous sulfate, oxalic acid, or freshly dissolved metallic iron.

Instead of using another portion of the solution, the weighed precipitate from (**b**) may be dissolved by digestion on the water-bath in a covered beaker or flask with from ten to 20 cubic centimeters of a mixture of one part H_2SO_4, with four parts of water.

Deduct the per cent of ferric oxid obtained from the per cent of ferric oxid and alumina (**b**), and make corrections for filter ash and phosphoric acid, to obtain the per cent of alumina.

(**g**) *Determination of Phosphoric Acid.*—Evaporate from 100 to 200 cubic centimeters of solution A to about 25 or 30 cubic centimeters; nearly neutralize with ammonium hydroxid, add about ten grams pure crystallized ammonium nitrate, and gradually about 20 cubic centimeters molybdic solution ((1) (*b*), p. 11) and set in water-bath at a temperature of 40°. When the precipitate has settled sufficiently, draw out with a pipette about five cubic centimeters of the clear liquid, and test it by allowing it to run into five cubic centimeters of warm molybdic solution. If any precipitate be produced, the test liquid is returned to the main portion and more molybdic solution is added and the operation repeated until all the phosphoric acid is precipitated. After standing from eight to 12 hours at a temperature not above 40°, the ammonium phosphomolydate mixture is filtered and the phosphoric acid determined as magnesium pyrophosphate. It is recommended to redissolve the magnesium ammonium phosphate precipitate in acetic acid, after it has been washed once or twice, and reprecipitate with ammonia and a fresh quantity of magnesia mixture, giving the usual time for the separation of the precipitate. If there be any residue of phosphates remaining on dissolving the phosphomolybdate in ammonia, or the magnesium ammonium phosphate in acetic acid, this residue is dissolved in a little hydrochloric acid, neutralized with ammonium hydroxid and precipitated with molybdic solu-

tion, and the phosphomolybdate obtained added to the main quantity.

(*b*) *Optional Provisional Method.*—Proceed as in (*a*) "until all the phosphoric acid is precipitated," and then finish the determination as follows:

After standing for three hours at a temperature not above 50°, filter on a small filter, wash with water until two fillings of the filter do not greatly diminish the color produced with phenolphthaleïn by one drop of standard alkali. Place the filter and precipitate in the beaker and dissolve in standard alkali, add a few drops of phenolphthaleïn solution and titrate with standard acid, one cubic centimeter of which equals 0.0005 gram of phosphoric acid (P_2O_5).

(**h**) *Provisional Method for Determining Phosphoric Acid.*—Ten grams of the air-dried soil, passed through a sieve of one millimeter mesh, are placed in a small kjeldahl flask marked at 250 cubic centimeters. From 20 to 30 cubic centimeters concentrated sulfuric acid and approximately 0.7 gram yellow oxid of mercury are added, the contents of the flask well mixed by shaking, and oxidizing over the open flame, as in the determination of nitrogen, for an hour. After cooling, about 100 cubic centimeters of water, five cubic centimeters of concentrated hydrochloric and two cubic centimeters nitric acid are added, and the mixture reboiled to oxidize the iron, cooled, the volume completed to the mark with water, and the contents of the flask filtered through a dry, folded filter paper. One hundred cubic centimeters of the filtrate are placed in a flask of about 450 cubic centimeters capacity, strong ammonia added until a permanent precipitate is formed, which is dissolved by the addition of about seven cubic centimeters of nitric acid, and the mixture boiled until clear. The flask is removed from the flame and cooled at room temperature for exactly two minutes, 75 cubic centimeters molybdate solution added, and the flask placed in a water-bath kept at 80° for 15 minutes, shaking vigorously four or five times meanwhile. After removing from the bath, the flask is allowed to stand for ten minutes until the precipitate has settled, and the supernatant liquid is poured onto the filter paper under pressure, the

precipitate being partially brought upon the paper. The flask and precipitate are thoroughly washed with ammonium-nitrate solution, and the precipitate separated either by decantation or on the filter paper. The flask is placed under the funnel, the precipitate is dissolved in ammonia, and the phosphoric acid estimated by usual processes.[44]

(i) *Determination of Sulfuric Acid.*—Evaporate 100 or 200 cubic centimeters of solution A nearly to dryness on a water-bath to expel the excess of acid; add 50 cubic centimeters of distilled water; heat to boiling and add from two to three cubic centimeters of a solution of barium chlorid, and continue the boiling for five minutes. When the precipitate is settled, pour the liquid on a tared gooch, treat the precipitate with from 15 to 20 cubic centimeters of boiling water, and transfer to the filter and wash with boiling water, at first slightly acidified with a few drops of hydrochloric acid, and finally with pure water, till the filtrate is free from chlorids. Dry the filter, ignite, and weigh as barium sulfate, which multiplied by 0.34331 equals SO_3.

(j) *Determination of Potash and Soda.*—Treat the filtrate from (j) with ammonium hydroxid exactly as in (b). Evaporate the filtrate and washings to dryness, heat below redness, until ammonium salts are expelled, dissolve in about 25 cubic centimeters of hot water, add five cubic centimeters of baryta water, and heat to boiling; let settle a few minutes, and test a little of the clear liquid with more baryta water to be sure that enough has been added. When no further precipitate is produced, filter and wash thoroughly with hot water. Add ammonia and ammonium carbonate to complete the precipitation of the barium, let stand a short time on the water-bath, filter and wash to precipitate thoroughly with hot water, evaporate filtrate and washings to dryness in a porcelain dish, expel ammonium salts by heat below redness, take up with a little hot water, add a few drops of ammonium hydroxid and a drop or two of ammonium carbonate, let stand a few minutes on the water-bath, filter into a tared platinum dish, evaporate to dryness on the water-bath and heat to dull redness, until all ammonium salts are expelled and the residue is nearly or

[44] Bulletin No. 43, Division of Chemistry : 58-60.

quite white. The heat must not be sufficient to fuse the residue. The weight of the residue represents potassium and sodium chlorids. Determine the potassium present with platinum chlorid in the usual manner. The sodium chlorid is obtained by subtracting potassium chlorid thus found from the total weight of the two chlorids.

Instead of the filtrate form (j), a fresh aliquot portion of soluiton A may be evaporated to dryness, redissolved in water and treated directly with milk of lime as in ash analysis; but without previous addition of barium chlorid.

5. *Determination of Acid-Insoluble Materials.*—The residue from 4 (a) may be analyzed by the usual methods for silicates. If it be desired to determine the silica soluble in alkalies, the residue must be dried at 100° and an aliquot portion removed before ignition for treatment with sodium carbonate solution. Another aliquot portion, or the rest of the residue, is ignited and weighed.

6. *Determination of Total Alkalies.*—Determine in a separate portion of the soil by J. Lawrence Smith's method[45]; or, preferably, determine by this method the alkalies in the insoluble residue from 4 (a) and add the amount obtained from the hydrochloric acid solution.

7. *Identification of Lithium, Caesium, and Rubidium.*—The salts of these elements are occasionally found in very small amounts in soils. Their agricultural uses are still in question, and their amount is too small to admit of quantitative estimation. A qualitative examination may be made by the spectroscope with the water-soluble materials evaporated to dryness and dissolved with two or three drops of hydrochloric acid or with the alkaline chlorids separated as in 4 (k) or 6.

8. *Determination of Total Nitrogen in Presence of Not More Than a Trace of Nitrates.*—From seven to 14 grams of the soil are placed in a small kjeldahl digesting flask of about 250 cubic centimeters capacity with 30 cubic centimeters of strong sulfuric acid, or more, if necessary, and 0.7 gram of yellow oxid of mercury and boiled for an hour. The residue is oxidized with potassium permanganate in the usual way. After cooling the

[45] Crookes's Select Methods, 2nd edition : 28-40.

flask is half filled with water, vigorously shaken, the heavy matters allowed to subside and the supernatant liquid poured into a flask of from 1,000 to 2,000 cubic centimeters capacity. This process is repeated until the ammonium sulfate is practically all removed and the digestion flask is a little more than half full and the ammonia then distilled in the usual manner. Where more than a trace of nitrates is present the methods of procedure, described in volume second of this manual, are to be followed.

9. *Determination of Carbon Dioxid.*—In from five to ten grams of the sample in any of the usual forms of apparatus determine the carbon dioxid evolved on treatment with an acid by increase of weight in the potash absorption bulbs.

10. *Determination of Humus.*—Ten grams of the sample are placed in a gooch, extracted wtih one per cent hydrochloric acid until the filtrate gives no reaction with ammonia and ammonium oxalate, and the acid removed by washing with water. The contents of the crucible (including the asbestos filter) are then washuntil the filtrate gives no reaction with ammonia and ammonium oxalate, and the acid removed by washing with water. The contents of the crucible (including the asbestos filter) are then washed into a glass-stoppered cylinder with 500 cubic centimeters of four per cent ammonia and allowed to remain, with occasional shaking, for 24 hours. During this time the cylinder is inclined as much as possible without bringing the contents in contact with the stopper, thus allowing the soil to settle on the side of the cylinder, and exposing a very large surface to the action of the ammonia. The cylinder is then placed in a vertical position and left for 12 hours, to allow the sediment to settle to the bottom. The supernatant liquid is filtered and the filtrate must be perfectly clear and free from turbidity; evaporate an aliquot portion, dry at 100° and weigh. The residue is then ignited and again weighed. The humus is calculated from the difference in weights between the dried and the ignited residues.

11. *Determination of Humus Nitrogen.*—Digest the soil with two per cent hydrochloric acid and wash as nearly free of acid as possible with distilled water. Extract the humus with a three per

cent solution of sodium hydrate and determine nitrogen in the extract in the usual way.

12. *Statement of Results.*—All results of soil analysis are to be calculated as per cent of the soil dried to constant weight in the water oven, and are to be stated in the following order:

Insoluble matter	}
Soluble silica	}
Potash (K_2O)	
Soda (Na_2O)	
Lime (CaO)	
Magnesia (MgO)	
Manganese oxid (MnO)	
Ferric oxid (Fe_2O_3)	
Alumina (Al_2O_3)	
Phosphorus pentoxid (P_2O_5)	
Sulphur trioxid (SO_3)	
Carbon dioxid (CO_2)	
Water and organic matter	
Total	
Humus	
Ash	
Phosphorus pentoxid	
Silica	
Nitrogen (organic)	
Hygroscopic moisture	
Moisture absorbed at t°	

PART SEVENTH

METHODS OF STUDYING THE ACTIVITY OF NITRIFYING ORGANISMS IN THE SOIL.

456. Introductory Considerations.—The detailed methods for estimating nitrogen in the forms of nitric and nitrous acids belong properly to the second volume of the work which is devoted to a study of fertilizers and manures. Since the existence of these forms of nirtogen in the soil is transient and their production practically continuous they naturally fall into the class of fertilizers rather than of permanent soil constituents. The organisms to which these bodies owe their chief origin in the soil are, however, so general that a study of that part of their activity which results in the formation of nitrates, nitrites and ammonia belongs properly here. It is scarcely necessary to state that this part of the work is in no sense a treatise on soil bacteria. Reference will be made here only to those features of the subject which are necessary to the comprehension of functions of the soil, from a chemical point of view, in producing fertility. For detailed studies of bacterial life and descriptions of methods of culture and isolation, reference is made to the standard works on bacteriology.

457. Organic Nitrogen in the Soil.—With the exception of the small quantities of nitric acid added to the soil directly in rain and snow, the whole supply of this substance, so necessary to plant life, is derived from the oxidation of the nitrogen of the atmosphere or of the organic nitrogen supplied to the soil by decaying animal and vegetable matters.

These products are either stored as the results of past nitrification or are formed synchronously with their consumption by the growing plant. Nitrogenous compounds are present in the soil as organic vegetable or animal remains and as humus. All vegetable and animal material deposited in or on the soil contains more or less of these proteid or nitrogenous matters while the amount of

nitric acid supplied in this way is probably represented entirely by the quantity in the organism of the plant or animal and unabsorbed at the time of its death. In other words it is not demonstrated that nitrates or nitrites are in any sense a special product of plant growth save in the case of nitrifying organisms themselves which are supposed to be of a vegetable nature. Animal organisms do not in any sense assimilate nitric nitrogen.

With most plants, the quantity of proteid nitrogen which they can deliver to the soil is in no case greater than the sum of organic and nitric nitrogen supplied in their food and they can therefore be regarded only as the carriers and conservers of this substance. On the other hand there are some plants, notably those belonging to the leguminous family, which permit of the development on their rootlets of colonies of bacteria which have the faculty of rendering atmospheric nitrogen available for plant growth. Whether or not there exist bodies other than the micro-organisms mentioned which are capable of directly oxidizing and fixing atmospheric nitrogen is still an unanswered question. It is not probable, however, that the difficult task of oxidizing atmospheric or free nitrogen would be accomplished in nature in only one way. In fact it has already been established that organisms do exist which are capable of oxidizing free nitrogen in a manner wholly independent of other plant life and to produce weighable quantities of nitric acid when developed in media of mineral matters and pure carbohydrates to which free nitrogen has access. It is, therefore, fair to assume that the fixation of free nitrogen is a function of chemical activity quite independent of ordinary plant life and that the leguminous plants take no further part in this process than that of providing in their radical development a favorable nidus for the growth of the nitrifying organisms.

By the action of denitrifying organisms a portion of the nitrogen of nitric acid is constantly restored to a free state, a far larger portion, perhaps, than is fixed in the atmosphere itself by the action of electricity. Were it not, therefore, for the activity of the nitrifying ferments the stores of nitrogen available for growing plants would constantly become less. Instead of this being the case, however, it is probable that the contrary is true and that,

by a wise system of agriculture, the total nitrogen at the disposal of plants may become greater and greater in quantity.

It will prove of interest here to refer to the first publication of the Department of Agriculture in so far as it has come to the attention of the author making reference to the nitrifying organisms.[46]

"The sources of nitrogen in crops are the nitrates and ammonia salts, which are seldom present in large quantities and should be used on or generated in the soil as rapidly as crops require them. The process of nitrification whereby inert or unassimilable nitrogen becomes converted into nitric acid is thus of great importance to agriculturists. This (action) is due to a minute *bacterium* present in all soils whereby the humus and ammonia are oxidized and the nitrogen (thereof) converted into nitric acid. This process does not take place unless the soil is moist and has free access of air and some base, generally lime, is present with which the nitric acid can combine. Nitrification is thus most active in summer and ceases apparently in winter."

458. Development of Nitric and Nitrous Acids in Soils.—Owing to the solubility of nitrates there can be but little accumulation of them in soils in those countries where there is any considerable amount of rain-fall. On the other hand in arid regions there may be found extensive deposits of nitrates. The occurrence of a certain quantity of nitrates in the soil, however, is essential to the growth of plants. Until within a few years little was known of the origin of nitric acid in the soil. The presence of nitrates in drainage waters was well established, likewise the consumption of nitric acid by the growing plant, but the method of its supply was unknown. In a general way it was said that the nitric acid came from electrical action and the oxidation of the albuminous bodies in the soil, but without specifying the manner in which this change takes place. The researches of Hellriegel, Schlösing and Müntz, of Springer, Winogradsky, Frankland, Warington and others have demonstrated the fact that this oxidation is caused by bacteria and that the nitrates formed can be consumed and destroyed

[46] Department of Agriculture, Annual Report, 1885; 165.

by other species of this organism. In the one case the process has been called nitrification and in the other dentrification.[47]

The influence of these low organisms both in producing fertility in a soil and maintaining it in a state of fertility is of the highest importance.

459. Conditions Necessary for Nitrification.—In order to properly understand the reasons for many of the steps in investigating a soil for nitrifying organisms, it will be useful to state the general conditions on which nitrification depends.

The nitrifying organism, like every other one, first of all feels the necessity for food. In general, food which is given to microbes of all kinds consists of some organic matter together with the addition of mineral substances necessary to growth. These substances in general are phosphoric acid, potash, and lime. Of these articles of bacterial food phosphoric acid seems to be the most important. With the nitrifying organisms, however, it has been found that the organic matter can be omitted. In fact, as will be seen further on, the omission of organic matter supplies the best condition for the proper isolation of the organisms. In other words some forms of the nitrifying organisms have the property of subsisting wholly on mineral substances, *i. e.*, are true vegetables.

The presence of oxygen is also necessary to the growth of the common nitro-organisms. In an atmosphere deprived of oxygen or in which the oxygen is reduced to a very low percentage, the process of nitrification is retarded or stopped as the oxygen diminishes or disappears.

There are, however, some groups of nitrifying organisms which are able to assimilate considerable quantities of nitrogen in the absence of free oxygen. These are known as anaerobic ferments.

The presence of a base with which the nitrous or nitric acid formed may unite is also essential to the proper conduct of the process. For this reason the nitrification should take place in a

[47] Comptes rendus, 1877, **84** : 301 ; 1879, **89** : 891 ; Journal of the Chemical Society (Trans.), 1878, **33** : 44 ; 1879, **35** : 429 ; 1884, **45** : 637 ; American Chemical Journal, 1882-83, **4** : 452 ; Proceedings of the American Association for the Advancement of Science, 1892, **41** : 93 ; Annales de l'Institut Pasteur, 1890, **4** : 213, 257, 760 and **5** : 92.

solution which is feebly alkaline or in the presence of a base which can be easily decomposed so that no acidity can be established. Calcium carbonate is a base well suited to favor the nitrifying process and its presence in a soil favors the rapid oxidation of proteid matter. The mistake must not be made, however, of supposing that an excess of alkali would favor nitrification. The contrary is true. A slight excess of alkali may prevent nitrification altogether when it is due to the common organisms present in an arable soil. It may be that in soils charged with alkali a different organism exists which is capable of exercising its functions when the alkali is in excess.

The temperature to which the nitrifying body is subjected is also a matter of importance. The nitrifying organisms have the property of remaining active at lower temperatures than most bodies of their class. On the contrary, their action is retarded and destroyed by high temperatures. The most favorable temperature for nitrification is about that of blood heat; *viz.*, 37°. At 50° the organism shows very little activity and at 55° its activity ceases altogether. Nitrification, however, according to Warington, cannot be started in a solution if the initial temperature is 40°.

Desiccation has the same retarding influence on nitrification that a high temperature has. Even thoroughly air-drying a soil may paralyze its nitrifying qualities.

Darkness is also necessary to the proper progress of nitrification. In a strong light, the activity of the organism is very much diminished or destroyed altogether. A bright light like sunshine may even stop nitrification which has set in.

460. Determination of Nitrifying Power of Soils.—In studying the distribution of the nitrifying organisms in a soil the general method of procedure is based on the production of nitrification in a convenient solution by the organisms present in a given sample of soil. If the solution seeded with the given portion of soil remain unaffected, it will show that there were no nitrifying organisms present in the seed used. On the other hand, the vigor of the nitrifying process when once it is started, may be taken as an evidence of the number and activity of the organisms in the soil, a sample of which was used for seed.[48]

[48] See paragraph 467.

461. Effect of Potassium Salts on Rate of Nitrification.—Dumont and Crochetelle have described some experiments to determine the effect of potassium salts alone and in combustion with lime on nitrification.[49]

A soil rich in vegetable mold (18.5 per cent of humus and 0.29 per cent of lime) was treated with varying amounts of potassium sulfate and carbonate and kept for 20 days at 25°. In the untreated soil the amount of nitric acid produced was 25 parts per million. When potassium carbonate was applied in quantities of from one-tenth to six per cent the amount of nitric acid increased from 47 parts per million to 438 parts when four and one-half per cent of the potassium salt were used. Larger quantities caused a decrease in the amount of nitric acid produced. Very little effect, on the contrary, was produced by the action of potassium sulfate. When one-half per cent was employed the quantity of nitric acid formed rose to 50 parts per million, while with quantities as high as five per cent it fell below the normal; *viz.*, 25 parts per million.

When calcium carbonate was added to the soil in conjunction with potassium sulfate there was a marked increase in the amount of nitrogen oxidized. The activity of potassium sulfate in promoting nitrification is therefore increased by the presence of the calcium salt, potassium carbonate and calcium sulfate being formed.

These results show that the nitrification was promoted by alkaline salts or neutral carbonates, while a neutral sulfate was practically ineffective.

462. Production of Nitrous and Nitric Acids.—In the following pages the study of the methods of isolating the nitrous and nitric ferments will be considered as one process, the final isolation of the two classes of bodies being the result of their synchronous cultivation in appropriate media. The special process of the production of ammonia by oxidation is not so well-known, and will therefore be described in brief.

It is now generally conceded, as shown by the comparative ex-

[49] Comptes rendus, 1894, **118** : 604.

periments conducted in the Bureau of Chemistry, given in paragraphs 467 and following, that the action of the nitrous organism is precedent to that of the nitric, but the two processes go on so nearly together as to prevent the accumulation of any large quantities of the lower salt in the soil.

Whether or not the formation of ammonia precedes that of nitrous acid is still a subject for experimental demonstration. Chemically, both nitrous acid and ammonia may be produced by the reduction of nitric acid, but the ammonia thus formed may pass through the nitrous acid state. In nature, the reverse of this process may be the customary method.

463. **Production of Ammonia in the Soil by the Action of Microbes.**—It is highly probable as intimated above, that organic nitrogen in the soil in passing into the form of nitric acid exists at some period of the process in the form of ammonia.

Marchal has isolated and studied some of these ammonia-making bacteria.[50] Bacillus mycoides is the most active of these organisms. It occurs constantly in surface soils and is present in the air and in natural waters. In decomposing albumen it produces a strongly alkaline solution due to ammonium carbonate. Organic carbon, during this process, is converted chiefly into carbon dioxid, but small quantities of formic, propionic, and butyric acids are also produced. Any organic sulfur which is present is converted into acid. No hydrogen or nitrogen is eliminated in a free state. While slight alkalinity is favorable to the development of this bacterium, yet it may be propagated in a feeble sulfuric acid solution when the acid is less than one per cent.

The greatest activity of this organism is manifested at 30°. Below 5° and above 42° no ammonia is produced. The bacillus will not develop in an atmosphere of hydrogen or carbon dioxid, except in solutions of organic matter and nitrate. In addition to its action on egg albumen it decomposes other proteid bodies as well as leucin, tyrosin, creatin, and asparagin. It, however, does not oxidize urea, nor does it develop in solutions of ammonium salts and nitrates, except as mentioned above. When soluble carbo-

[50] Bulletin de l' Académie royale de Belgique, 1894, [3], **25** : 727; Journal of the Chemical Society, London, 1894, **66**, part 2 : 248.

hydrates are present, acids are formed. It is concluded from these experiments that the final oxidation of organic nitrogenous matter is preceded by its conversion into ammonium carbonate.

464. Summary of Statements.—All nitrogenous matters which would be naturally present in the soil may become subject to nitrification when the proper conditions are supplied. Munro has also succeeded in nitrifying ethylamin, thiocyanates, and gelatin, urea, asparagin, and the albuminoids of milk and rape-seed.

The chief products of nitrification are ammonia, nitrous or nitric acid, carbon dioxid, and water. The ammonia and nitrous acid may not appear in soils as the final products of nitrification, as the nitric organism attacks the latter at once and converts it into nitric acid. Nitrous acid and ammonia may also be produced in soils as one of the retrograde steps in denitrification.

To summarize the conditions necessary for proper nitrification it may be said that first, the proper material must be supplied; *viz.*, an organic or inorganic nitrogenous compound capable of oxidation. In the second place, the medium must be faintly alkaline, the temperature must not be too high, nor too low, the nitrifying organisms must have abundant food, and the process must take place in the dark.

465. Order of Oxidation.—It is quite definitely determined that activity of the ammoniacal and nitrous organisms is the first step in the process, since the nitric organism appears to have no power whatever to oxidize proteid compounds; while, on the other hand, the nitrous organism can not, in any case, complete the conversion of nitrous into nitric acid.

The conditions which permit certain organisms to oxidize free nitrogen have not been definitely determined. The presence of such bodies in the tubercles attached to the rootlets of certain leguminous plants has been established. These organisms are not able to exert their activity in the soil alone and will be described in the second volume of this work. Lately, Winogradsky has isolated from the soil a nitrifying organism which is capable of converting free nitrogen into forms suited to nourish plant growth. This organism is cultivated in dextrose with careful exclusion of all nitrogen, save that which exists in the air carefully freed of every trace of ammonia or oxidized nitrogen.

Under the influence of the growth of this organism the sugar undergoes a butyric fermentation, and nitrogen in an oxidized form is assimilated in an amount apparently equal to about one five-hundredth of the sugar consumed.

This result leads Warington[51] to remark that it is a fact of extraordinary interest, both to the physiologist and chemist, that a vegetable organism should be able to acquire from the air all the nitrogen it needs.

466. The Nitrification of Ammonia.—The same organism which converts organic nitrogen into nitrous acid acts also on ammonia and its compounds with a similar result. In fact, the formation of ammonia may be regarded as one of the stages on the road from albuminoid to nitric nitrogen.

Data have been collected by Schlösing on the nitrification of ammonia taking place in arable soil, tending to show that this phenomenon is accomplished without appreciable loss of nitrogen in the gaseous state.[52] This, however, does not hold good when the quantity of ammonium carbonate introduced into the earth is largely increased. In two experiments, conducted by Schlösing, with a larger quantity of ammonium carbonate, the loss of nitrogen was very notable. In certain conditions the production of nitrous acid may take place, and it is interesting to know whether the appearance of nitrites has any influence on the disengagement of free nitrogen. In order to determine this question a solution of calcium nitrite was prepared by decompositing silver nitrite with calcium chlorid. From the results of the experiments made it was seen that the nitrites were only the results of a retarded and partially incomplete nitrification. They, are, moreover, thus an obstacle to the normal work of the nitrifying organisms. It is also established that when they are present a disengagement of gaseous nitrogen takes place, whether the nitrites are formed during the progress of the experiment, or whether they were originally present. However, it is not best to say that the nitrites themselves have been the cause of the disengagement of the nitrogen. It may happen that the disengagement of the nitrogen and

[51] Chemical News, 1893, **68** : 175.
[52] Comptes rendus, 1889, **109** : 883.

the presence of nitrites are simply simultaneous and due to one and the same cause. The destruction of nitrates in the midst of reducing agents furnishes, according to the nature of these bodies and the circumstances, nitrous acid, nitrogen dioxid, nitrogen protoxid, free nitrogen, and even ammonia.

This destruction of nitrates and the appearance of oxids of nitrogen and of free nitrogen are more likely to be due to the presence of a separate dentrifying ferment as pointed out by Springer than to have arisen in the manner mentioned above by Schlösing. In the present state of our knowledge, moreover, we can hardly regard the presence of nitrites as an obstacle to complete nitrification. On the other hand, it seems to be well established that the production of nitrites or ammonia is a necessary step between organic nitrogen and nitric acid.

467. **Activity of the Nitrifying Organisms in Soils.**—To determine the activity of the nitrifying organisms in soils—that is, those of the nitrous and nitric classes—the author in conjunction with Ewell, in 1895, devised the plan which is described below. The object of the investigation was to determine the activity of the ferments in the soil without attempting in any way to count or isolate them. In other words, it is purely an analytical process to ascertain a certain property of the sample under examination. By collecting samples at the same time and under the same conditions from widely separated localities the comparative nitrifying properties of soils may be determined.

468. **Sampling Tubes.**—The tubes described in 75 are conveniently used for the present purpose. The rubber caps over the ends should be of different colors to distinguish before removing the cutting from the blunt end. The blunt end is closed with a plug of cotton and a similar plug is placed in the bottom of the cap of the cutting end in such a way that it is not disturbed when the cap is removed at the time of sampling. This plug takes the place of the rubber ball used to prevent the cutting of the rubber cap by the sharp edge of the tube.

The caps are put in place and the whole apparatus sterilized by heating for a proper time to the temperature of boiling water. The tubes are then ready without further manipulation for use as above described.

Fig. 83. **Sampling Tubes for Determination of Nitrifying Power.**

Fig. 84. Glass Hood for Seeding Nitrifying Cultures.

The appearance of the tubes, as prepared for sending the sample by mail, are shown in Fig. 83.

The quantity of soil transmitted in the tubes described above is much greater than is needed for seeding the cultures, but it is necessary to get that amount in order to obtain a representative sample. Each sample is thoroughly mixed before removing the portions for the inoculations. For this purpose a number of small erlenmeyer flasks are plugged with cotton and sterilized in a hot-air sterilizer. Each tube is then carefully opened and its contents pushed into one of the sterile flasks with the aid of a large sterilized glass rod of a diameter slightly less than the internal diameter of the tube. These manipulations are conducted under a glass hood, Fig. 84, with the customary precautions for the transfer of materials from one piece of apparatus to another without contamination with atmospheric organisms.

Before the flasks are again closed, the lumps of soil are broken up and thoroughly mixed with the fine soil by means of a sterilized glass rod or a sterilized platinum spatula.

469. Collecting Samples.—By following carefully the directions given below, it will be possible to secure small samples of soil free from other micro-organisms than those normally contained therein:

The tubes and their rubber caps are carefully sterilized and should not be removed from their cloth envelopes until the moment of sampling. After the sample has been secured and the cap replaced on the tube, the latter should be immediately enclosed in the cloth sack and labeled with one of the tags therewith enclosed. The samples should represent at least two kinds of soil, in one instance the cultivated soil, which is most characteristic of plots, and in the second place a virgin soil of the same type. The virgin soil may be either soil which has been covered with grass or in forest. The spots at which the sampling is to be done are selected, and the tags for each tube are prepared beforehand so as to avoid delay at the time of sampling. A pit with straight walls is dug, the sides of which are at least two feet wide and even three feet would be better. The pit is at least 42 inches deep. One of the sides having been made perfectly smooth, and without

allowing the loose fragments from the top to fall down and adhere to the walls below, the spots at which the samples are to be secured are marked with a tape line at the following points; *viz.*, 3, 15, 27, and 30 inches, respectively, below the surface. Beginning at the bottom point, scrape off the surface of the wall over an area slightly larger than that of the end of the sample tube by means of a spatula, which, just previous to use, has been held for a moment or two in the flame of an alcohol or other convenient lamp. The sample tube having been removed from its sack, it will be noted that the end covered with black rubber is the one which is to be held in the hand, and this black rubber cap should be first removed, being careful not to extract the plug of sterilized cotton which closes the end of the tube. Holding the tube firmly by the end, the fingers extending only about two inches from the end, remove the light colored cap and push the tube with a turning motion into the side of the pit at the point where the surface has been removed with the sterilized spatula. When this is properly done the tube will be filled with a cylinder of soil equal to the length of the part of the tube penetrating the wall of the soil. The tube is withdrawn, the light rubber cap first replaced, and then the black one. The light rubber cap is held in the hand during the process with the mouth down so that no dust or particles of soil are permitted to contaminate its inner walls. For the same reason after the removal of the light rubber cap the brass tube should be carefully preserved from dust or fragments, the open end, that is the cutting end, being held downward until ready for use. After one tube has been filled, capped, replaced in the sack and labeled, the spatula should be again sterilized and samples taken in regular order until the top one is finished. The tubes are sent by mail.

470. **The Culture Medium and Seeding.**—The solution of ammonium sulfate and nutritive salts used as the culture medium for this series of investigations has the following composition:

	Grams.
Ammonium sulfate	0.942
Potassium phosphate	1.000
Magnesium sulfate	0.0
Calcium chlorid	trace
Distilled water	1000 cc.

These are the so-called "chemically pure" reagents usually at hand in the laboratory. The solution does not contain more than the merest traces of organic matter.

One hundred cubic centimeters of this solution are placed in each of several sterilized Erlenmeyer flasks of, from 150 to 200 cubic centimeters capacity. The cotton plugs are returned to the flasks, glass caps are placed over them, and the flasks thus charged are sterilized in a steam sterilizer in the usual manner, being heated for the proper length of time on each of three successive days. Some freshly precipitated and carefully washed calcium carbonate is also prepared and sterilized in similar flasks, after mixing with such a quantity of water that five cubic centimeters of the well-shaken mixture contains in suspension a little more than 0.2 gram of calcium carbonate.

It is believed to be impracticable to weigh the portions of soil used for seeding the cultures without contaminating them with organisms contained in the air and adherent to floating dust. Moreover, since the moisture content of the samples varies considerably, it is thought that a measured quantity is more satisfactory than one weighed. Portions of each sample are therefore transferred to each of three culture flasks by means of a sterilized platinum spoon holding between 0.4 and 0.5 gram of a moderately moist soil. To each of two of the three flasks seeded with a given sample, there is added by means of a sterilized pipette approximately 0.2 gram of the sterilized calcium carbonate referred to above. No calcium carbonate or other agent for the neutralization of the nitrous and nitric acids formed, and the sulfuric acid set free as the nitrification progressed, is added to the third flask seeded with each sample of surface soil. From this series of cultures containing no neutralizing agent the data in regard to the influence of acidity upon the activity of the nitrifying organisms referred to were obtained[53].

In the case of each sample from a greater depth than three inches only two cultures are prepared and to both of these calcium carbonate is added.

[53] Journal of the American Chemical Society, 1896, 18 : 475.

471. **Temperature Considerations.**—When a thermostat of sufficient dimensions to hold all the cultures is not available, the culture flasks are placed in a dark closet, the temperature of which varies with that of the laboratory air. The fluctuations are unfortunately very considerable, and their effect on the rate of nitrification is very marked, as will readily be seen on examination of the data presented below. The readings of a maximum and minimum thermometer, kept in the culture closet, are recorded each day. Series of cultures were seeded, as above described, on May 3, 9, 18, 27, June 5, 19, 26, July 13, 19, September 10, October 12, and November 15, 1895. Temperature charts are made to record the maximum and minimum daily temperature throughout the period of eight weeks following each of the dates of seeding.

472. **Progress of Nitrification.**—At the end of each week following the seeding of the cultures, each culture is tested for the purpose of ascertaining the amount of nitrification accomplished during the preceding seven days. Diphenylamin and concentrated sulfuric acid are the reagents used for this test. At the end of each succeeding week throughout the observation period of eight weeks the amounts of nitrous and nitric acids are determined. For these tests the appropriate portion, and no more, of the culture fluid is removed from each culture flask and transferred to the tube or evaporating dish in which the test is made. A separate sterilized pipette is used for the removal of the liquid from each flask.

473. **Methods of Testing for Nitrous and Nitric Nitrogen.**—Diphenylamin and concentrated sulfuric acid are used for the purpose of ascertaining the time at which nitrification begins because they react with both nitrous and nitric acids. The depth of the blue color produced by the action of the nitrates or nitrites upon diphenylamin in the presence of concentrated sulfuric acid varies considerably with the temperature and strength of the acid. For the purpose of obtaining comparable results it is necessary that a uniform method of manipulation should be used, and after a number of experiments the following process was adopted:

To one cubic centimeter of the culture solution to be tested which is transferred from a culture flask to a dry test tube by means of a sterilized pipette, there is added one drop of a

solution of diphenylamin in four cubic centimeters of concentrated sulfuric acid. The tubes are well shaken and immediately placed in a water-bath at 80° and kept therein at this temperature for 15 minutes. Until this method of manipulation was adopted, it was difficult to obtain agreeing results when duplicate tests of known solutions were made.

474. **Method for the Determination of Nitrous Nitrogen.**—After trials of various methods the naphthylamin and sulfanilic acid method was adopted. The method of manipulation is substantially that in use in water analysis with several important modifications which will be described. The principal difficulty arises from the fact that in the latter part of the culture period of eight weeks the quantity of nitrites developed by many of the soils is so great that in some of the solutions the color produced is very deep and even results in the production of a precipitate. This difficulty is obviated by the following method of manipulation.

Two and one-half cubic centimeters of the culture fluid are transferred to a graduated cylinder by means of a sterilized measuring pipette. A large quantity of distilled water is kept at hand to which has been added the proportion of naphthylamin, sulfanilic and acetic acids usually employed in the determination of nitrites in water. The portion of culture fluid contained in the graduated cylinder is diluted at first to about 100 cubic centimeters and the dilution continued as the color develops, being conducted more rapidly in the case of those tests which show the presence of greater amounts of nitrous nitrogen.

The standard solutions for comparison containing known quantities of nitrous acid are prepared simultaneously with the unknown solutions. At the end of 20 minutes or half an hour the observation is begun and is conducted in 50 cubic centimeter nessler cylinders, the comparison being made by means of transmitted light. A comparison camera similar to those used in iron and steel laboratories for carbon determinations is employed. The total volume of the solution and the number of the standard tube which matches a given unknown solution are recorded and the process is complete with the exception of the calculation.

It will be noted that acetic acid is used as the acidulating re-

agent for this test. Moderately strong acidulation is required to prevent precipitation of the colored reaction product, particularly when the color is very dark. Strong acidulation with acetic acid is found most satisfactory for this purpose.

475. **Method for the Determination of Nitric Nitrogen.**—For this determination a modification of the picric acid method is employed. Phenol-sulfonic acid is used, prepared according to the direction of Gill.[54] The culture medium contains only traces of chlorin, therefore precautions are unnecessary to eliminate errors arising from the presence of this substance. The test is conducted as follows:

Two and a half cubic centimeters of culture liquid are transferred to a small procelain dish by means of a sterilized measuring pipette. One drop of sodium carbonate solution is added, and the liquid evaporated to dryness. The residue is treated with the proper quantity of phenol-sulfonic acid reagent which is brought in contact with every part of the residue by means of a short stirring rod. Ten cubic centimeters of water and three cubic centimeters of strong ammonia water are added, and the unknown solutions are compared in a nessler cylinder with a standard solution prepared at the same time. Any suitable colorimeter may be used for this comparison.

476. **Statement of Results of the Investigations.**—In most cases the agreement in the rate and magnitule of the nitrification is very satisfactory. Any difference in the mean results from two different soils may, therefore, be attributed to original differences in the soil *in situ*.

In the sample supplying the data in the accompanying chart, it is seen that nitrification has only just commenced at the end of the first period of seven days, the quantity of nitrous and nitric acids present being, approximately, a half of one part per million in each of the duplicate samples. The first sample, represented by the heavier continuous line, shows a more marked nitrification at the end of the second week, the total quantity of nitrous acid present being two parts per million, and the total quantity of both

[54] Determination of Nitrates in Potable Water. Journal of the American Chemical Society, 1894, **16** 122; Mason, Examination of Water, 1899: 43-44.

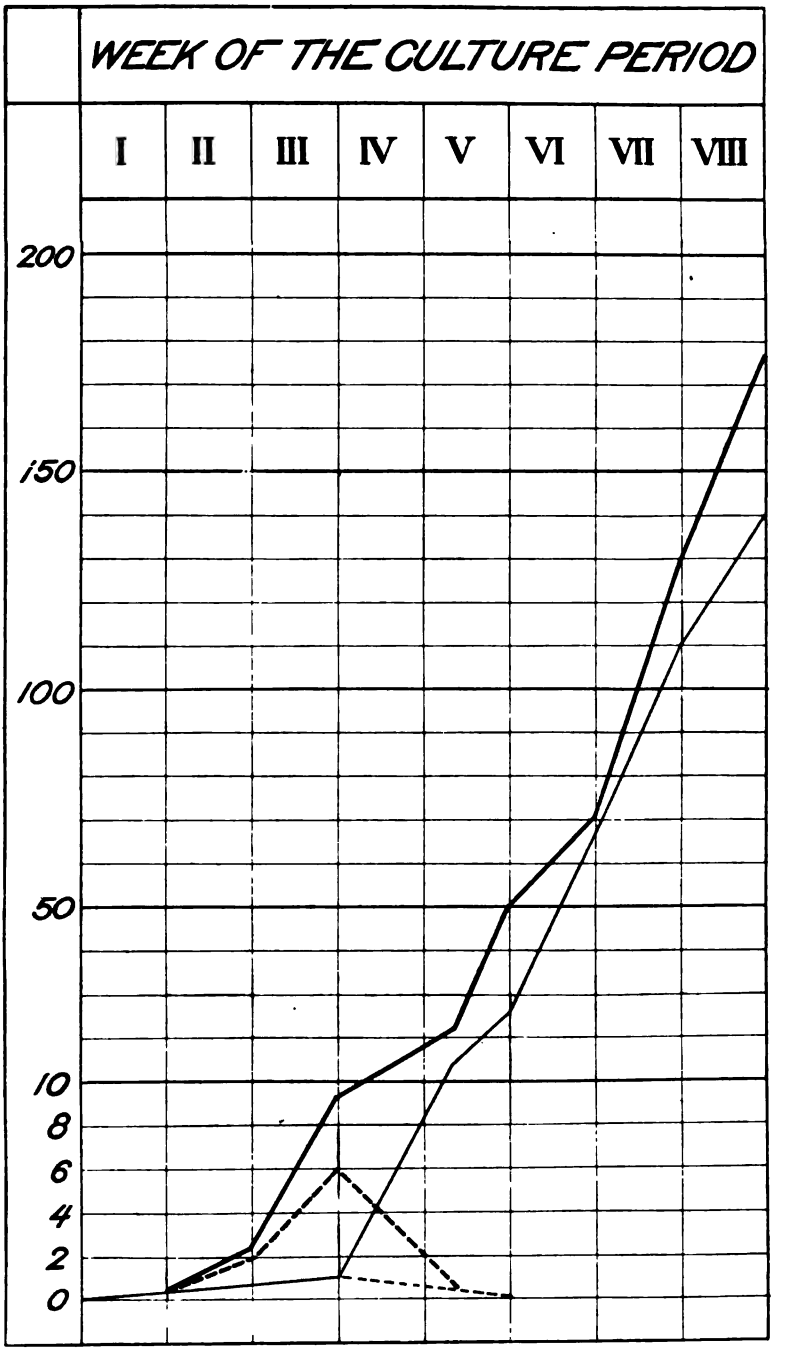

Chart showing parts per Million of Nitric and Nitrous Acids, Paragraph 476.

acids being, approximately, 2½ parts per million. A duplicate sample meanwhile shows a total nitrification of only about one part per million. At the end of the third week the nitrous acid has risen in the first sample to six parts per million, and the two acids to a little more than nine parts per million, showing, approximately, the presence of three parts per million of nitric acid and six parts per million of nitrous acid in the first sample, while the second sample has only still a little over one part per million of nitrous and nitric acid. At the end of the fourth week the nitrifying ferment begins to gain upon the one producing the nitrous acid, both in the orignial and duplicate sample. In the original sample the nitrous acid has fallen to two parts per million, while the total acids have risen to almost eleven parts per million, showing nearly nine parts per million of nitric acid. In the duplicate sample there is approximately a half part per million of nitrous acid and eight parts per million of both acids, showing 7½ parts per million of nitric acid. At the end of the fifth week the nitric ferments have gained a distinct victory. They have consumed all of the nitrous acid which has accumulated and convert any which is till formed at once into nitric condition. The original sample shows 50 parts per million of nitric acid and no nitrous acid. The duplicate sample shows 25 parts per million of nitric acid and no nitrous acid. From this point up to the close of the experiment at the end of the eighth week there is no accumulation of nitrous acid whatever, and the nitrification in the two samples progresses almost at the same rate. At the end of the period the original sample has 170 parts per million and the duplicate sample 140 parts per million of nitric acid.

477. **Effect of Acidity on Rate of Nitrification.**—In connection with the above investigations a study of the effect of acidity on the speed of nitrification was conducted.[55] The studies were made on 22 virgin and 22 cultivated soils from 22 States and Territories.

The following results were obtained:

[55] Ewell and Wiley, Journal of the American Chemical Society, 1896, 18 : 475.

SUMMARY OF RESULTS.

In	5	cases	0	part	per	million	of	nitrogen	was	nitrified
In	1	case	11	parts	"	"	"	"	were	"
In	2	cases	14	"	"	"	"	"	"	"
In	4	"	15	"	"	"	"	"	"	"
In	5	"	18	"	"	"	"	"	"	"
In	10	"	20	"	"	"	"	"	"	"
In	5	"	22	"	"	"	"	"	"	"
In	6	"	25	"	"	"	"	"	"	"
In	1	case	28	"	"	"	"	"	"	"
In	1	"	40	"	"	"	"	"	"	"
In	1	"	42	"	"	"	"	"	"	"
In	1	"	70	"	"	"	"	"	"	"
In	1	"	130	"	"	"	"	"	"	"
In	1	"	170	"	"	"	"	"	"	"

Averages: Of 44 tests 28 parts per million of nitrogen were nitrified
" Of 34 " 20 " " " " " " "

In general, it was noticed that where the acidity was sufficient to consume per liter from three to four cubic centimeters of normal alkali, nitrification stopped. The quantity of nitric acid produced was in general proportional to the carbonates in the sample. The two showing 130 and 170 parts per million are samples from Alabama, containing considerable quantities of carbonate of lime. These data show the great importance of the function of carbonate of lime in nitrification in the soil.

Burri and Stutzer have found that the organisms from different soils assumed an almost uniform nitrifying power after a number of cultivations in an artificial medium.[56] This fact leads to the suggestion that valuable data would be obtained by inocculating the sterilized soils with the same organism and noting the results over long periods.

478. Occurrence of Nitrifying Organisms.—According to the observationst of Schlösing and Müntz the nitrifying organisms are widely distributed.[57] Arable soil containing considerable humus seems to be the medium in which they grow most freely and in which they accomplish their most important functions. Sewage waters are also rich in nitrifying ferments, and, in fact, all waters containing organic matter. They are also found in running

[56] Central-Blatt für Bakteriologie, 1896, **2** : 105.

[57] Comptes rendus, 1879, **89** : 891.

waters but not in great numbers. They affect chiefly the surface of bodies, and especially are found on the bottom of culture-flasks.

These authors have not found the nitrifying organisms in normal air. They could not seed sterilized flasks with nitrifying organisms by admitting air freely. The absence of these ferments from the air is explained by reason of their sensitiveness to desiccation.

The method used by Schlösing and Müntz for the separation of the organism consisted in the preparation of original and subcultures in sterilized solutions containing nitrifiable matters. The proof of isolation was assumed when a given subculture contained only one kind of organism as seen with the microscope. The appearance of this organism, as described by the authors, was that of the later isolations by Warington and Winogradsky, but the method used could hardly now be regarded as decisive.

479. **Warington's Culture Medium.**—The solution recommended by Warington for the culture and isolation of the nitrifying ferments has the following composition:

	Milligrams
Ammonium chlorid	80
Sodium potassium tartrate	80
Potassium phosphate	40
Magnesium sulfate	20
Calcium carbonate, in excess, about	200
Pure bacteria-free water, to make one liter.	

480. **Apparatus and Manipulation.**—The experiments are conducted in short, wide-mouthed bottles. The initial volume of the solution in each bottle is 100 cubic centimeters, and the bottle should be of such size as to give a depth of liquid of from three to five centimeters.

The neck of the bottle is closed with a plug of cotton and this is protected from dust by tying over it a cap of filter paper. Arranged in this way, filtered air has free access to the solution. The bottle with the solution thus protected is placed in a water-oven and kept near the temperature of boiling water for from six to eight hours to destroy any organisms present. When cool, the solution is ready for use.

The calcium carbonate used should be prepared by precipitation and added in a moist state. The calcium carbonate solution should be added after the sterilization of the liquid, the precipitated carbonate being boiled just before it is added.

Preparation of Seed.—The seed employed to start the nitrification should be a small quantity of fresh soil, usually about one-tenth of a gram. If a previously nitrified solution be used for seed it should be thoroughly shaken and about one cubic centimeter of the solution removed for seeding the new bottle.

In introducing the nitrifying liquor into the bottle the plug should be lifted slightly and a small pipette inserted by means of which the liquor is added. The operation should be carried on in a room perfectly free from dust and to which no one but the operator has access. The greatest care should be exercised to prevent any particles of matter entering the solution except that which is purposely added. In withdrawing the liquor from the nitrifying solution, cotton wool should be pressed around the top of the pipette so that the entering air may be filtered before admission to the interior of the bottle. The pipette which is used should be kept in boiling water until it is required for use. After use it should be washed and replaced in boiling water until again required.

After seeding, the bottles should be placed in a dark cupboard and exposed to the ordinary temperature of the laboratory. If a higher or stated temperature be desired, the bottle should be placed in a metal box the temperature of which can be regulated to any degree.

Test of the Commencement of Nitrification.—The beginning of the nitrification can be determined in a solution by testing it with diphenylamin. One cubic centimeter of the solution withdrawn as above indicated, is placed in a small beaker, a drop of solution of diphenylamin sulfate in sulfuric acid added, and then two cubic centimeters of concentrated sulfuric acid and the contents of the beaker well shaken. The development of a violet-blue color shows the presence of nitric or nitrous acid. This test will detect one part of nitric nitrogen in 20 millions parts of water.

Determining the Progress of Nitrification.—The progress of

nitrification is determined by repeated examinations for ammonia by nesslerizing, and for nitrous acid with metaphenylenediamin. Each experiment is made with five cubic centimeters of the solution withdrawn as above indicated and placed in test-tubes, always of the same size. The reaction with the nessler solution is then made by adding it in the usual way. The colorations are recorded as, trace, small, moderate, considerable, large, and abundant.

If the change produced by the organism consisted in the formation of nitrites only, the ammonia in the original solution would fall from *large* to *trace,* while the nitrous acid would increase from *trace* to *large.* If the nitrification consisted in the production of nitrates only, the ammonia would diminish without any corresponding production of nitrous acid. In mother solutions which contain ammonium carbonate instead of sulfate, it should not be forgotten that the ammonia might gradually disappear owing to the volatilization of the carbonate without any corresponding production of free nitrites or nitrates. The total disappearance of the ammonia in the above experiments shows the completion of the process.

481. **To Determine the Distribution of the Nitrifying Organism in the Soil.**—The principle on which the determination of the distribution of the nitrifying organism in the soil depends, rests upon seeding the growth solutions with samples of soil taken at different depths and carefully protected from the time of sampling until the time of seeding from any admixture of accidental organisms. The method of study used in the Bureau of Chemistry has already been described.

The method of Warington is described below.[58] The samples of soil are secured by digging a pit of convenient depth usually from eight to ten feet. A fresh surface is then cut on one of the sides of the pit at the spot selected for sampling. This surface is scraped with a freshly ignited platinum spatula. The spatula should then be washed, re-ignited, and cooled, and a small portion of the soil, at the depth required, detached with the spatula and

[58] Journal of the Chemical Society (Trans.), 1884, **45** : 645.

transferred at once into one of the growth bottles already described.

The growth solution best suited for the purpose contains four cubic centimeters of urine per liter. Each bottle should also contain some freshly precipitated calcium carbonate. In sterilizing urine solutions the calcium carbonate should be added before the heating instead of afterwards. The quantity of soil taken for each seeding should be about one-tenth of a gram.

Inasmuch as the cotton stopper has to be lifted to introduce the soil, opportunity is given for the entrance of any organisms floating in the air. Experience, however, has shown that air free from soil dust very seldom contains nitrifying organisms. The seeded bottles are placed in a dark cupboard of moderate temperature as already described.

482. Sterilized Urine Solution.—The sterilized urine solution used for the determination of the distribution of the nitrifying organisms in the soil, is made by diluting four cubic centimeters of healthy urine to one liter, adding some freshly precipitated calcium carbonate, stoppering with cotton wool and heating for several hours at the boiling temperature of water.

As a result of Warington's experiments it was shown that the nitrifying organism in the soil did not exist, at least in portions of one-tenth of a gram, to a greater depth than 18 inches. In only one case was nitrification produced from a sample of soil taken at a greater depth and this may have been due to the accidental introduction of organisms from other sources. It may be assumed that any long delay in the commencement of nitrification under favorable conditions, implies the presence of a very limited quantity of organisms in the solution. Thus a comparative study of the period of incubation and the progress of nitrification in solutions seeded with soils taken at different depths or at different places, becomes a fair index of the number and vitality of the nitrifying organisms contained therein.

483. Depth to Which Micro-Organisms are Found.—As seen above, Warington found very few organisms below 18 inches. Koch states that at the depth of about one meter, the soil is nearly free from every kind of bacteria.[59] These observations have been

[59] Jahresbericht über die Agrikultur-Chemie, 1881, New Series, **4** : 43.

corroborated by other observers, and by the author's experience, and it is now believed that not many active bacteria are found in soils to a greater depth than about three meters.

It is evident from the nature of the experiments above described that the nitrifying processes go on almost exclusively in those portions of the soil which are subject to cultivation, while in the subsoil and below the processes of nitrification are either retarded or arrested. Any stores of nitrogenous matter, therefore, in an insoluble state, resting in the subsoil, are preserved from oxidation and consequent waste until such time as they may be removed to near the surface.

484. Isolation of the Nitrous and Nitric Organisms in the Soil.— The action of the organisms which produce nitrification either in form of nitrites or nitrates, having been thoroughly established, and the method of testing the soil therefor given, it remains to describe a method by means of which these orgainsms in the soil may be isolated and obtained in a state of purity. The difficulties attending this process are extremely great on account of the similarity of the two organisms. The first attempts to make pure cultures of the two separate organisms were attended with but little success. Following the brilliant researches of Winogradsky the technique of the process has been greatly improved by many workers. It is not desirable here to trace the later development of these methods but rather to give a brief description of the earlier investigations which are most valuable from an historical point of view and because they so well illustrate the principles on which the investigation rests.

According to Winogradsky the method of culture on gelatin so long practiced is not to be relied upon.[60] It is not difficult to eliminate by this process the organisms which grow rapidly in gelatin and which mature their colonies in two or three days, but where they require from eight or ten days to produce a colony the method is unsuccessful. In fact, by the gelatin process as it was at first practiced, much was owing to chance, but sometimes by a happy accident a pure nitro-bacterium might be isolated.

Formerly it was considered that a liquid could be regarded as sterile if it gave no growth upon gelatin. It has, however, now

[60] Annales de l'Institut Pasteur, 1891, **5** : 92.

been demonstrated that a liquid may contain large numbers of nitro-bacteria and still produce no growth upon gelatin. However, for the organisms which accompany the nitro-bacteria in soils, it is regarded as certain that if no growth on gelatin is produced by them they are absent. Therefore in the case of a solution which has been seeded with a soil, if it can be brought to such a state as to produce no growth on gelatin, it may be safely assumed that it contains no bacterial organisms save those which are capable of producing nitrites or nitrates. Therefore, if such a solution produce nitrification and at the same time no growth upon gelatin, it may be considered as a proof of the isolation of the nitro-organisms from all others.

This method was also worked out independently by Percy and Grace Frankland.[61]

These views are provisionally advanced and are not regarded as definitely established. Strictly speaking, the proof of seeding gelatin is not sufficient alone because the absence of growth can not be regarded as the exclusive privilege of the nitro-bacteria. Such might be the case sometimes for an accidental mixture of microbes, introduced with any given sample of soil into the cultures, but the criterion is not absolute. Microbes, for example, of a sulfurous or ferruginous nature may be cited, for which the gelatin layer is not only unfavorable but even fatal. It may thus happen that there may be eliminated from the solution all that will grow upon gelatin without freeing it from some special kinds of cultures, refractory like the nitro-bacteria, but which might reappear if they should be resown in some favorable nutritive solution. On account of this fault in the process, Winogradsky has been impressed with the necessity of bringing out a better method.

In using the gelatin media it is necessary to find the one that is suited to nourish these organisms, which would evidently be the way promising the greatest success. This having been found, and those organisms which produce colonies being easily recognizable, a great step towards the solution of the problem will have been made and the more so as the medium would be at the same

[61] Philosophical Transactions of the Royal Society, 1890, **181** : 107.

time absolutely unfavorable to other forms of microbes. On account of the slow degree of development of the nitro organisms, all others would probably have opportunity to grow and strengthen to their exclusion, unless these interfering organisms could be completely removed.

485. The Culture Solution.—The culture-solution, first proposed by Winogradsky, has the following composition:

To ten grams of gelatin or one part of agar-agar in 100 cubic centimeters of water add one-tenth of a gram of potassium phosphate, five-hundredths of a gram of magnesium sulfate, a trace of calcium chlorid, and half a gram of sodium carbonate. The solution being sterilized in the usual way by heating, there are added to it a few cubic centimeters of a sterilized solution containing two-tenths per cent of ammonium sulfate. Although such a solution has been supposed to be very favorable to nitro-organisms, no definite results were obtained.

The non-success of this method led Winogradsky to adopt a nitrifying solution which absolutely excluded all organic substances. Instead of using an animal or vegetable gelatinous substance he used one of a mineral nature, first proposed by Graham and developed by Kühne[62]. Two of these gelatinous mineral substances were considered; *viz.*, the aluminum hydroxid and the hydrate of silica. The latter was finally chosen.

486. Preparation of the Mineral Gelatinous Solution.—The soluble glass which is found in commerce is generally of a thick, sirupy consistence. It is first diluted with three times its volume of water. One hundred cubic centimeters of this liquid are poured with constant stirring into 50 cubic centimeters of dilute hydrochloric acid and the mixture placed in a dialyzer. It is useless to employ a standard solution of silica. All that is necessary is to submit to dialysis a liquid with an excess of acid and sufficiently dilute not to be exposed to the danger of being spontaneously gelatinized in the dialyzer. The dialyzer is left for one day in running water and two days in distilled water, often renewed. The solution is ready for use when it is no longer rendered turbid on the addition of silver nitrate, showing that the

[62] Zeitschrift für Biologie, 1890, New Series, 9 : 172.

hydrochloric acid (sodium chlorid) has been entirely extracted. The solution is sterilized by boiling, and preserved in a glass flask closed with a plug of cotton.

More recent instructions by Winogradsky for preparing the gelatinous silica recommend dialyzing the soluble glass after treatment with hydrochloric acid in a parchment tube.[63] The proportions of silicate and acid are 100 cubic centimeters of the silicate solution (1.06 specific gravity) and 100 cubic centimeters of hydrochloric acid (1.1 specific gravity). With a dialyzing tube placed two days in running water and one day in distilled water frequently changed it will be found that the acid is completely removed. One hundred cubic centimeters of the residual liquor giving no reaction for hydrochloric acid are concentrated to 20 cubic centimeters. When cold there is added one cubic centimeter each of a solution of ammonium sulfate and of sodium carbonate, together with corresponding quantities of the other nutrient salts commonly employed. The ammonium sulfate should never exceed from two to two and a half, and the sodium carbonate four parts per thousand. To the flask containing the above substances is added one drop of the seed-liquor, which may be a soil water or a drop from some previous culture. The flask is shaken and the mixture poured into a low circular glass dish which is covered by one slightly larger in diameter (Petri double dish). To the liquid in the dish is added a drop of a cold saturated solution of common salt, and it is then stirred with a platinum spatula. The addition of the salt greatly favors the setting of the jelly. The jelly may set in from two to three hours, but a longer time secures better results in the end.

In employing these preparations as seed, after the organisms have grown, it is absolutely necessary to use the isolated cellules and not the aggregated masses (zoöglœæ). The latter are rarely free of foreign germs which adhere to their gelatinous envelope. Since the zoöglœæ can not be broken up by any artificial means it is necessary to await their spontaneous disintegration in order to separate the mobile monads. The opalescence of the culture-liquid is a sure index of this separation.

[63] Archives des Sciences biologiques á St. Pétersbourg, 1892, 1 : 107.

The particles of mineral gelatin to be used as seed for nitrifying are best taken as follows:

A glass tube is drawn out immediately preceding the operation, until the end is as fine as a hair. The surface of the mineral gelatin is magnified by means of a dissecting microscope and the preparation table is so arranged as to give a perfect support to the right hand which should hold the filament of glass. The smallest colony is then pricked with the needle and the end of the glass is broken and dropped into the flask which is to be seeded. The seed is thus selected in as small a particle as may be desired, only a few cells, but it can always be ascertained with certainty that some of the particles have been obtained by this operation.

The method of cultivation on mineral jelly is considered by Winogradsky an important resource in the study of the nitrifying organisms. It removes the chief difficulties heretofore existing in discovering and characterizing these organisms among the innumerable micro-organisms of the soil. The long series of cultures necessary to separate the organisms are rendered unnecessary. By directly introducing a little of the earth into the silicic jelly the active organisms in nitrification can be at once discovered. It is preferable, however, as indicated below, to previously produce a nitrification in an aqueous solution by a trace of earth and to take from it the seed for impregnating the solid medium. In order to show at once a proof of its nitrifying character, it is only necessary to take a small bit of the mineral jelly, the size of a grain of rye, and to throw it into a little sulfuric acid which has been treated with diphenylamin. There is at once formed a blue spot equal in intensity to a saturated solution of anilin blue.

In regard to the growths which nitro-organisms make in a medium of the kind described, they are far from being so marked as are those produced by ordinary micro-organisms.

A nitro-bacterium is not capable of the energy of growth which is recognized for the greater number of microbes. The colonies contained in the gelatin always remain small. The largest among them are just visible to the naked eye like white points. Along the striae, on the contrary, there is formed quite a thick white crust. To the naked eye, in general, there is nothing very char-

acteristic in the formation of colonies in a medium of this nature. But this impression changes altogether when the placques are examined with a low magnifying power. The colonies, especially those of the interior surface, reveal then an aspect so curious as to be well remembered when once seen.

This mineral gelatin, as has already been noticed, is very unfavorable to the growth of microbes other than nitro-bacteria and becomes altered only under the action of the air. If the placques be carefully preserved from desiccation the culture of these organisms can be continued for several weeks. Although they do not seem to increase, the colonies, as well as the jelly, are still in a good condition at the end of that time. Nevertheless the expectation that this medium would prevent the formation of any foreign organism has not been realized. Some of the organisms which accompany the nitro-bacteria in soil, also grow upon the silicic jelly; but they do not form colonies, properly so-called, and their growth is extremely slow. They generally make their appearance before the nitro-bacteria and spread exclusively upon the surface in form of white spots, so transparent that without careful examination they would not be discovered. Having reached a certain size the spots do not change during entire weeks. This circumstance renders the operations of isolation somewhat delicate, but does not prevent them.

487. Preparation and Treatment of the Solution to be Nitrified.—The organisms having been grown on the siliceous gelatin in the manner described they are tested for their nitrifying power as follows:

The mineral solution which is to be nitrified with the above preparation is composed of four-tenths gram of ammonium sulfate, half a gram of magnesium sulfate, one-tenth gram of potassium phosphate, a trace of calcium chlorid, six-tenths to nine-tenths gram of sodium carbonate, and 100 cubic centimeters of distilled water.

The sulfates with the calcium chlorid on the one hand, and the phosphate and carbonate on the other, are dissolved separately and the two solutions sterilized separately and mixed after cooling. The seeding is then done as described above.

488. Isolation of the Nitrous and Nitric Organisms.—Instead of proceeding immediately to the isolation of special organisms in the soil, the preliminary period of purification is prolonged by Winogradsky by allowing the free growth of all the organisms which can be maintained in the ordinary medium.[64]

The composition of the culture solution employed is as follows: One thousand parts of distilled water, one part of potassium phosphate, half a part of magnesium sulfate, and a trace of calcium chlorid. Each flask receives besides this some magnesium carbonate, freshly washed with boiling water and added in slight excess.

The flasks thus charged are sterilized, and there are added two cubic centimeters of a solution of two per cent of ammonium sulfate, which when added to 15 or 20 cubic centimeters of liquid give from two to two and a half parts per thousand. They are then seeded with soil. The reasons for this preliminary treatment are as follows: First, all the observations upon the enfeeblement of the oxidizing power of these organisms have been made upon cultures seeded simply by the fresh soil, and in cultures derived therefrom. In the second place, the existence of the two forms, one nitrous and the other nitric, prevents at once the isolation of a single organism.

Samples of soil from Europe, Africa, Asia, Australia, and America, were used for seed in the experiments. First, the cultures were made by seeding with a small quantity of each of these samples of soil, and each one of these cultures served at a point of departure for a series of subcultures. The temperature of the cultures should be kept constantly at 30°.

The method of following the nitrification adopted by Winogradsky is essentially that of Warington, the percentage of ammonia remaining at any time being determined by nesslerizing. To detect the presence of nitric acid the nitrous acid is decomposed by boiling with ammonium chlorid in excess, or with area, and then diphenylamin is used as a reagent. By treatment with ammonium chlorid and boiling, the ammonium nitrite is resolved into free nitrogen and water as indicated by the equation

[64] Annales de l'Institut Pasteur, 1891, 5 : 577.

$NH_4NO_2 = N_2 + 2H_2O$. Or the total oxidized nitrogen may be estimated by the Schlösing method or by any of the standard methods hereafter given. The nitrous acid is then determined by potassium permanganate and the nitric acid by difference.

A great difference is to be noted between freshly taken earth and that which has been kept for a long while, especially when sealed. With fresh earth from near the surface a mere trace is sufficient to produce nitrification. With samples of earth which have been kept for a long while and thoroughly dried, several grams must be added in order to secure perfect nitrification. The period of incubation with the samples of earth ranges from three to 20 days. The beginning of the phenomenon is revealed by the appearance of nitrous acid, of which the quantity is increased very rapidly, but in the end it disappears and is transformed into nitric acid.

489. Statement of the Results.—The method of stating the results of examination of soils for nitrifying organisms conducted as above is illustrated by the following example:

Soil from Zürich.—The culture was seeded on the 11th of October, with one gram of soil. On the 20th of October the nitrous acid had reached its maximum of intensity and there was no ammonia left. On the 29th of October the nitrous acid remained almost stationary and there was hardly any nitric acid present. On the 1st of November the reaction for nitrous acid began to decrease. On the 5th of November the reaction for nitric acid was very intense. On the 11th of November the nitrous acid had all disappeared except a mere trace.

The above order of phenomena was observed with all the samples of soil tried, from which it is concluded with certainty that nitrifying organisms transplanted directly from their natural medium in the soil into a liquid easily nitrifiable produce at once nitrous acid in abundance. The phenomenon of nitrification is divided into two periods therefore, of which the first is devoted to the production of nitrites, and the second consists in the oxidation of the nitrites, and this does not commence until the total disappearance of the ammonia. Occasionally the formation and oxidation of the nitrites practically go on together, but never equally,

the oxidation of the nitrites being always sensibly behind their formation.

490. Method for Subcultures.—From the mother cultures described above, Winogradsky makes subcultures as follows:

The solution to be nitrified is prepared as in the mother cultures. The seeding is accomplished by adding a small quantity of the liquor of the mother culture after shaking. Subcultures can be made in this way to the seventh generation.

In respect of the oxidation of the nitrites the results may be entered as negative if they have not disappeared at the end of two months.

To determine whether the process of oxidizing the nitrites is in progress or not the total nitrous acid is estimated, and the process repeated at the end of eight or ten days. Should there be no diminution of the nitrous acid within this time it may be considered that the further oxidizing action is not taking place.

491. Use of a Solid Medium.—It may be justly claimed that the action of nitrifying organisms in a liquid is not to be compared with their action in a solid medium, such as a soil which is their natural habitat. It might be, therefore, that the inability of the nitrous organism to produce nitrates is due to the nature of the medium in which it is cultivated. Winogradsky in order to determine this question cultivated the organism in a solid medium of two kinds, first a silicate gelatin impregnated with an ammonium salt and second in sterilized earth. The silicate jelly is prepared as follows:

Mix a jelly of silica containing some ammonium sulfate with sterilized soil. The seeding is done with one of the subcultures which no longer has the power of producing nitrates.

In the case of the jelly the seeding is accomplished as follows:

A minute drop of a culture liquid is taken with a capillary glass tube and applied in striæ to different parts of the solid jelly; or a minute drop of the culture liquid may be mixed with the jelly before solidification. The Petri dishes in which these cultures are made can be preserved in a moist atmosphere, and thus the desiccation be easily prevented for a long time. From time to time

pieces of the jelly as large as a pea can be tested for the progress of nitrification.

Results.—The nitrous reaction, both in the prepared jelly and in sterilized soil, will appear in a few days. At the end of from seven to 12 days it will have attained its maximum intensity and will then remain stationary indefinitely. Sterilized soil has no power to generate the nitric from the nitrous ferment. The two organisms are, therefore, of different species.

After a few generations the power of producing nitrates seems to be lost although the nitrous ferment may still be active. This suppression of the power to oxidize the nitrites is not due to any pernicious influence of the culture-medium but to the condition of the successive solutions at the time of removing the seeding samples.

492. Microscopic Examination.—A small particle of the deposit in the culture-liquid is spread on a glass slide and dried. There is then added a drop of very dilute perfectly transparent malachite green solution; the zinc chlorid double salt or oxalate of bittermandelölgrün, or tetramethyldiamidotriphenylcarbinol. In about half a minute it is washed and colored by a very dilute solution of gentian violet which is left to act for some time. The cells then appear distinctly colored on a colorless background.

In examining nitrous cultures in this way under a moderate enlargement there are seen particles of material covered with scattered groups and massive zoöglœæ composed of cells which are, doubtless, identical.

By their round or roundish forms, by their relative size and especially by their numbers and uniformity they are at once distinguished from the other vegetations which are generally of a purely bacillus shape.

With the exception of some shreds of mycelium coming from some oidium in the soil the microscope reveals nothing but the organisms described. The microscopic appearance[65] of the nitrous ferment is shown in Fig. 85*a*.

The general conclusions of Winogradsky are:

[65] Annales de l'Institut Pasteur, 1891, 5 : 576, Plate XVIII.

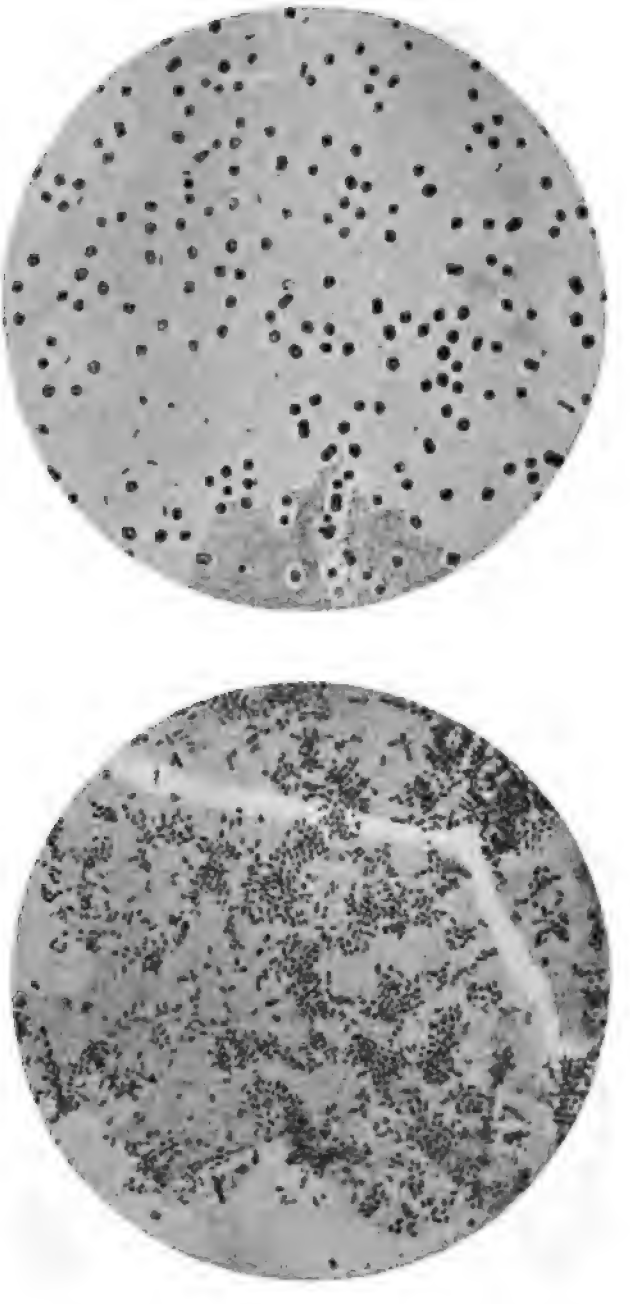

Figure 85*a*. (Upper figure.) Nitrous ferment prepared by Winogradsky from soil from Cito

Figure 85*b*. (Lower figure.) Nitric ferment prepared by Winogradsky from soil from Cito

1. Each soil possesses but one organism capable of oxidizing ammonia.

2. Soils from one locality have always the same kind of nitrifying ferment.

3. Soils from different and distant countries contain nitrifying organisms which differ from one another in some respects so much so that it may be necessary to distinguish a few species or even genera in these bodies.

493. Isolation of the Nitric Ferment in Soils.—The principle of the separation of this ferment as described by Winogradsky rests upon the fact that in culture solutions of a mineral nature free from ammonia the nitrous ferment will not grow, whereas if nitrite or nitrous acid be present the nitric ferment will grow.[66] In a few generations, therefore, the nitrous ferment will be entirely eliminated.

Solution employed:

	Grams.
Distilled water	1,000
Potassium phosphate	1
Magnesium sulfate	0.5
Calcium chlorid	trace
Potassium nitrite	0.22

To culture-flasks containing 100 cubic centimeters of the above mixture after sterilization about one-tenth gram of fresh soil is added. In favorable conditions the nitrous acid will disappear in about 15 days.

Subcultures are made by seeding fresh portions of the sterilized solution with one or two cubic centimeters of the mother culture. The operation is continued until the nitrous ferment is eliminated.

The organisms in the deposit in the culture-flasks are then subjected to microscopic examination in the manner already described for the nitrous ferment; or proceed as follows:

494. Culture on Solid Media.—Evaporate the liquid which has been employed in the culture of a nitrous ferment to one-third of its bulk. Gelatinize the residue by adding double its volume of the silicic acid solution prepared as already directed.

The jelly is placed in the glass vessels usually employed. The

[66] Annales de l'Institut Pasteur, 1891, 5 : 596.

seeding may be done with a few drops of a culture-liquid containing the nitric ferment as obtained above. The first reaction will appear in from eight to ten days. In about 45 days the nitrous acid in the jelly will have entirely disappeared. Two classes of colonies are noticed under the microscope. The first to appear are small colonies which never extend beneath the surface of the jelly. In cultures seeded with these colonies there is no oxidation of nitrous acid. The second class of colonies extends into the interior of the jelly. They are much larger than the first, of a yellowish-gray color and not spherical but rather lenticular in shape. Cultures seeded with these colonies will lose their nitrous acid in about ten days or two weeks.

The growth of these organisms in a liquid scarcely merit the name of cultures. The naked eye can usually distinguish no form of vegetation. The liquid remains clear, the surface is free from any film, no flocks are deposited. Colored and examined in the microscope the organisms found are so puny as to make doubtful their oxidizing power. There is an apparent contradiction between the powerful chemical action that these organisms can produce and their apparent deficiency in physical properties.

These organisms are best found by cultivating them in a very limpid solution. The bottoms of the culture boxes will be found covered with an extremely tenuous gelatinous deposit communicating to the glass a feeble grayish-blue tint. The culture bottle is inclined and the bottom scratched with a recently drawn-out capillary tube. The colonies rise in the tube together with a little of the liquid. The colonies are dried, mounted, and colored as already described and when examined with the microscope are found to be composed exclusively of masses of an organism of extreme minuteness.

The organism remains attached so firmly to the bottom of the culture bottle that it can be washed several times with pure water without danger of detachment and thus rendered more pure.

In old cultures which are sustained by new additions of nitrite an extremely transparent pellicle on the bottom of the flask can be distinguished. By shaking the liquid some fragments may be detached and made to float through the fluid. With a little care

and patience these flocks can be captured, mounted, and colored. Since they show the nitric organism in its natural state their preparations are of the greatest interest.

The best preparations are made by coloring with malachite green and gentian violet and then coloring again with magenta. Afterwards the preparation is washed with warm water at 50°-60° which takes almost the whole of the color from the gelatinous matter. The cells are then clearly presented colored a reddish violet on a rose background. These organisms[67] are shown in Fig. 85*b*.

The figure shows the cells united by a gelatinous membrane and grouped in small dense masses composed often of a single layer of organisms. The cells are generally elongated, rarely regularly spherical or oval. Their mean length does not exceed half a micromillimeter and their thickness is from two to three times less.

The difference in form of the nitrous and nitric ferments is very marked and leaves no doubt of the existence of these two forms which are as distinct as could be desired in microbic discrimination.

495. Dilution Method of Warington.—The method pursued by Warington in preparing pure cultures of the nitrifying ferment is based on the well-known principle of dilution which may be expressed as follows:[68] In a liquid containing bacterial ferments dilution may be practiced until a drop of the liquid may contain no more than a single organism of any one kind. If now proper solutions be seeded with single drops of this solution, some of them may give colonies of pure cultures of any given organism. The solution to be nitrified has the following composition:

	Parts.
Water	1000
Ammonium carbonate	0.25
Ammonium chlorid	0.50
Potassium phosphate	0.04
Magnesium sulfate	0.02
Calcium sulfate	0.02

[67] Annales de l'Institut Pasteur, 1891, **5**, Plate XVIII, Fig. 1.

[68] Journal of the Chemical Society (Trans.), 1892, **59** : 484.

The ammonium chlorid is added to prevent the precipitation of magnesium and calcium phosphates. The solution is kept in wide-mouthed, stoppered bottles to prevent the loss of ammonium carbonate, the bottles being only half full. About 100 cubic centimeters are used for each experiment. These bottles are sterilized and seeded with fresh soil in the ordinary way. They are then covered with paper caps and placed in a dark cupboard at a constant temperature of 22°.

Special Media.—A quantity of cultivated soil is exhausted of nitrates by washing with cold water under pressure. The soil is then boiled with water and filtered. The clear amber-colored solution obtained may be used instead of water in the above formula.

Solid Media.—(1) Ordinary ten per cent gelatin made with beef broth and peptone. (P)

(2) A ten per cent urine solution solidified with six per cent of gelatin. (U)

(3) A solution of one gram of asparagin, one-half gram sodium acetate, one-half gram potassium phosphate, two-tenths gram magnesium sulfate, two-tenths gram calcium sulfate, and one liter of water solidfied with six per cent gelatin. (As)

Other solid media may also be employed for the purpose of favoring, as much as possible, the growth of the nitrifying organisms.

The first culture in the ammonium carbonate solution given above, is always made by seeding with a little unmanured cultivated soil. Subcultures are seeded from this mother culture by seeding new solutions with a few drops of the original. In all cases tried by Warington the subculture produced only nitrous fermentation while the original cultures produced the nitric fermentation.

496. **Microscopic Examination.**—The microscopic examination of the organisms formed is conducted as follows:

The cover glasses previously sterilized are placed at the bottom of the culture-flask. At the end of the nitrification the liquid is removed with a pipette and the flask and cover glasses dried at 35°. The cover glasses are then removed and stained. The microscopic appearance of the organisms obtained by the previous

cultures show masses of corpuscles usually of oval shape and having a length generally exceeding one micromillimeter. An immersion objective giving a magnification of 800 diameters is suitable for this work.

Other forms of organisms are also met, the whole series being characterized as follows:

(1) The corpuscles already mentioned. Larger ones are frequently rough in outline resembling masses of sea-sand. The smaller oval corpuscles are regular in form.

(2) Some very small circular organisms often appearing as mere points and staining much more plainly than the preceding.

(3) A few slender bacilli, staining faintly.

All the cultures obtained by the above method give abundant growth on gelatin.

497. **Trials with the Dilution Method.**—One part of the third subculture in the ammonium carbonate solution described above, is mixed with 500 parts of thoroughly boiled water and one drop from a sterilized capillary tube is added to each of five bottles containing the sterilized ammonium carbonate solution. In Warington's experiments one of the five bottles was found to have nitrified after 41 days. After 91 days two more were nitrified. Two bottles did not nitrify at all. All three solutions which nitrified gave growths on gelatin. The growths took place more speedily on gelatins U and As than on P.

The organisms obtained on gelatin were seeded in appropriate liquid media but no nitrification was obtained.

A subculture from solution No. 2 of the first dilution mentioned above, was diluted to one one-thousandth, one ten-thousandth, one one-hundred-thousandth, and one one-millionth. Each of these dilutions was used for seeding with five sterilized solutions of ammonium carbonate, using the method of seeding above described. At the end of 190 days not one of these solutions had nitrified.

Warington supposed that the cause of failure in the method just mentioned might be due to the alkalinity of the ammonium carbonate. While this solution could be seeded in the ordinary way with fresh earth it might be that the faint alkalinity which it pre-

sented might prevent it altogether from action when the nitrifying agent was reduced to a few organisms.

He therefore changed the solution to one of the following composition:

	Parts.
Water	1000
Ammonium chlorid	0.02
Potassium phosphate	0.06
Magnesium sulfate	0.03
Calcium sulfate	0.03

The solution was divided in 20 stoppered bottles which were half filled. The bottles were divided into four series, A, B, C, D, each one consisting of five bottles, and these were respectively seeded with one drop from dilutions to one one-thousandth, one ten-thousandth, one one-hundred thousandth, and one one-millionth of a second subculture of No. 3 in the first dilution series.

After 115 days, nitrification had occurred in ten of the bottles. The other ten did not nitrfy at all. Each of the nitrifying solutions was spread on gelatin, P and U being employed. Growth took place far more easily on gelatin U than on gelatin P. Of the ten nitrified solutions there were three which gave no growth on gelatin U, either when spread on the surface or introduced into the substance of the jelly. There were therefore secured nitrifying solutions which did not contain organisms capable of growing on gelatin. The supposition is therefore fair that they were pure nitrifying organisms. These fresh, pure organisms had the faculty of converting ammonia into nitrous acid only and not into nitric acid.

With the organisms thus prepared a number of solutions of potassium nitrite containing phosphates and other mineral ingredients were seeded. In no case was any loss of nitrite found, which is proof that the solution contained no organisms capable of oxidizing nitrous acid. The organisms prepared as above, have the power of nitrifying organic substances containing nitrogenous bodies.

The organism isolated as described and examined under the microscope is seen to contain two forms. The first one is nearly spherical in shape, the corpuscles varying in size from mere points.

to a diameter of one micromillimeter. The form is very striking and easily stained. The second form is oval-shaped and attains a length distinctly exceeding one micromillimeter. Sometimes it is a regular oval and sometimes it is egg-shaped. This form is stained less easily than the preceding or spherical form.

498. Method of Staining.—The method of staining employed is as follows:

A drop of the culture-liquid is placed on a glass slide and mixed with the filtered stain by means of a wire. A cover glass is placed on the drop and allowed to stand for half an hour. It is then pressed down on the slide and the liquid which exudes wiped off and glue run around the cover glass. In this way the organism is stained in its own culture-fluid and can be seen in its true form without any possibility of the destruction of its shape by drying. The plate is bright and clear though colored.

If the preparation is to be mounted in balsam a drop of the culture is dried in the center of a cover glass. It is then placed for some minutes in dilute acetic acid to remove matter which would cause turbidity. The cover glass with its contents is then washed, dried, and stained for some hours in methyl violet.

499. Classification of Nitrifying Organisms.—The names proposed by Winogradsky for the various organisms are the following:

For the general group of microbes transforming ammonia into nitric acid, *Nitrobacteria.*

For the nitrous ferments of the Old World:

Genus, *Nitrosomonas:*

Species, *Nitrosomonas europaea.*

Nitrosomonas javanensis.

For the nitrous microbes of the New World:

Genus, *Nitrosococcus.*

Species, not determined.

For the nitric ferment:

Genus, *Nitrobacter.*

500. Nitrification in Sterilized Soil.—The process of nitrification in sterilized soil, when seeded with pure cultures, is determined as follows:

Preparation of Sample.—The fresh sample of cultivated soil is freed from pebbles and vegetable débris and reduced to as fine a state of subdivision as is possible in the fresh state. It is placed in quantities of about 800 grams in large crystallizing dishes.

One dish is set aside for use in the natural state, and the other, hermetically closed, is placed in a sterilizing apparatus and subjected to the action of steam for two and a half hours. This treatment is repeated three times on as many successive days.

Seeding of Sample.—Each of the two dishes is moistened with 50 cubic centimeters of pure water containing 500 milligrams of ammonium sulfate. The sterilized portion is then seeded with a preparation of the pure nitrous ferment, produced as before described. The seed is prepared by filtering a few cubic centimeters of the nitrous culture liquid through asbestos. The asbestos is well washed and then thrown into a flask containing a few cubic centimeters of sterilized water and well-shaken. The water carrying the filaments of asbestos is poured drop by drop on the surface of the soil in as many places as possible. The two dishes of soil are kept at an even temperature of 20° in a dark place. Winogradsky found that, treated in this way, the unsterilized soil produced only nitrates, while the sterilized portions produced only nitrites.[69]

501. Variation of the Determinations.—To vary the conditions of the experiment Winogradsky uses 12 flasks of the erlenmeyer shape, four having bottoms 12 centimeters in diameter, and eight of them five centimeters in diameter. In each of the four large flasks are placed 100 grams of fresh soil, and in each of the eight small flasks 25 grams. The eight small flasks are designated a, b, c, d, and a′, b′, c′, d′, and the four large flasks A, B, C, D.

The flasks a, b, c, d, and a′, b′, c′, d′, are placed in a stove at 30° for several days before use, while A, B, C, D, are kept at 20°-23° for the same length of time. The soil in the small flasks is, therefore, somewhat drier than that in the large ones.

The flasks are treated as follows:

a, a′, A, contain the soil as prepared above for control.

b, b′, B, are sterilized at 135° and seeded with a drop of the pure nitrous culture.

[69] Annales de l'Institut Pasteur, 1891, 5 : 605.

c, c', C, sterilized as above and seeded with a little of the unsterilized earth.

d, d', D, sterilized as above and seeded with pure nitrous and pure nitric cultures.

After sterilization there are added to the small flasks two cubic centimeters of a 20 per cent sterilized ammonium sulfate solution, and to the large ones six cubic centimeters. At the end of a month or six weeks the contents of the flasks are thrown on a filter and washed with cold water until a drop of the filtrate gives no blue color with diphenylamin. The respective quantities of nitrite and nitrate are then determined in the filtrates by the usual processes, which will be fully described further along.

502. Azotobacter of Byerinck.—Lipman has summarized the later investigations of the active soil nitrifying organisms and studied their relations to soil fertility.[70]

The entire group which is called Azotobacter is composed of rather vigorous bacteria producing no spores. The pure cultures grow in a great variety of media, preferably in those poor in nitrogen. They seem to be most vigorous at a temperature of 28°. Two species were isolated by Byerinck, namely, *Azotobacter Chroococcum* and *Azotobacter Agilis*. They grow on a great variety of media, particularly agar-agar, to which two per cent of acid potassium phosphate is added. They produce a green or red pigment with salts of organic acids and do not liquify gelatine.

Two additional species have been isolated by Lipman himself. A very large Azotobacter was named by Lipman in honor of the discoverer of the group *Azotobacter Beyerincki*.

Lipman also describes the nitrogen fixing power of the different species. The attempts which have been made so far to utilize the Azotobacter species for increasing the store of soil nitrogen have not been very successful. In the experiment of Lipman it is noticed that there is no decided gain in the inoculated soils over the non-inoculated. The determination, however, of this point is far from complete, and it is not beyond the sphere of probability that this species may be found to be useful in fixing and increasing the stores of nitrogen.

[70] **Twenty-fifth Annual Report of the New Jersey State Agricultural Experiment Station, 1904 : 237 et seq.**

503. Fixation of Free Nitrogen.—The fixation of free nitrogen in the symbiotic activity of certain nitrifying organisms with leguminous plants is not a problem suitable for discussion, except incidentally in this manual. The great importance of this action, however, to practical agriculture is well recognized. A recent discussion of the subject by Voorhees and Lipman gives a clear view of the importance of the subject and valuable knowledge of the technique of the methods of investigation.[71]

A further critical study of this subject has been made by Fischer,[72] who questions Beyerinck's classification of A. *agilis* and shows that lime is an indispensable element in the development of the Azotobacter, and that this element favors both nitrification and dinitrification. Lime is useful not only as a direct stimulant to nitrification, but also it is indirectly useful in promoting the production of humus which is a substance well suited to supply the Azotobacter with carbon.

504. Sterilization.—One of the chief requisites for success in the bacteriological investigation of soils is found in the thoroughness of the sterilizing processes. The value of cultures depends chiefly on the care with which the introduction of foreign germs is prevented. In the following description a mere outline of the method of sterilization is presented, while those who wish to study more carefully the details of the process are referred to the standard works on bacteriology.

Sterilization of the Hands.—It is important that the hands of the operator handling apparatus and materials for bacteriological work should be sterilized. The sterilization may be accomplished in the following way:

The nails are cut short and thoroughly cleaned with soap and brush. The hands are thoroughly washed in hot water with soap. After washing in hot water the hands are washed in alcohol and ether. They are then dipped in the sterilizing solution.

This liquid may consist of a three per cent solution of carbolic acid, which is the one most commonly employed. A solution of corrosive sublimate, however, is perhaps the best disinfectant. It

[71] Journal, American Chemical Society, 1905, **27** : 556.

[72] Journal für Landwirtschaft, 1905, **53** : 61.

should contain from one to two parts of the crystallized salt to 1,000 parts of water. It has lately been advised to use the sublimate in an acid solution. Acetic acid or citric acid may be employed, but hydrochloric acid is recommended as the best, in a preparation of one-half part per 1,000. For stronger solutions of sublimate containing more than a half per cent, equal quantities of common salt should be added. The solution should be made with sterilized water.

After dipping the hands in the sterilizing solution they are dried with a napkin taken directly from a sterilizing oven, where it has been kept for some time at the temperature of boiling water. Where only ordinary work in bacteriology is contemplated this sterilization of the hands is ont necessary. It is practiced chiefly in antiseptic surgery. The use of thin sterilized rubber gloves on the sterilized hands is an additional guaranty of safety, and excludes many dangers from infection.

Sterilizing Apparatus.—With platinum instruments the most effective and easiest way for sterilizing is to hold them in the flame of a bunsen until they are red hot. Steel and copper instruments can not be treated in this way without injury. They are best sterilized by submitting them to dry heat in a drying oven at a temperature of 150°-160° for two hours. Glass and porcelain apparatus can be sterilized best in the same way.

All apparatus and materials employed should be used in a space as free as possible from dust, so that any germs which might be carried in the dust can be excluded from the apparatus in transferring it from one place to another.

505. Methods of Applying Heat.—Sterilization by means of heat may take place in several ways.

First. Submitting the Materials to Dry Heat Without Pressure.—The temperature in sterilization of this kind may vary from the temperature of boiling water at sea-level to 160° obtained by an oil-bath or by an air-oven.

Second. Sterilization in a Liquid Under Pressure.—This form of sterilization may be effected by sealing the liquid in a strong vessel and submitting it to the required temperature. If the temperature required be greater than that of boiling water the vessel

can be immersed in a solution of some mineral salt which will raise the boiling-point.

Third. Sterilization in Steam Under Pressure.—This method of sterilization consists in placing the body in a proper receptacle

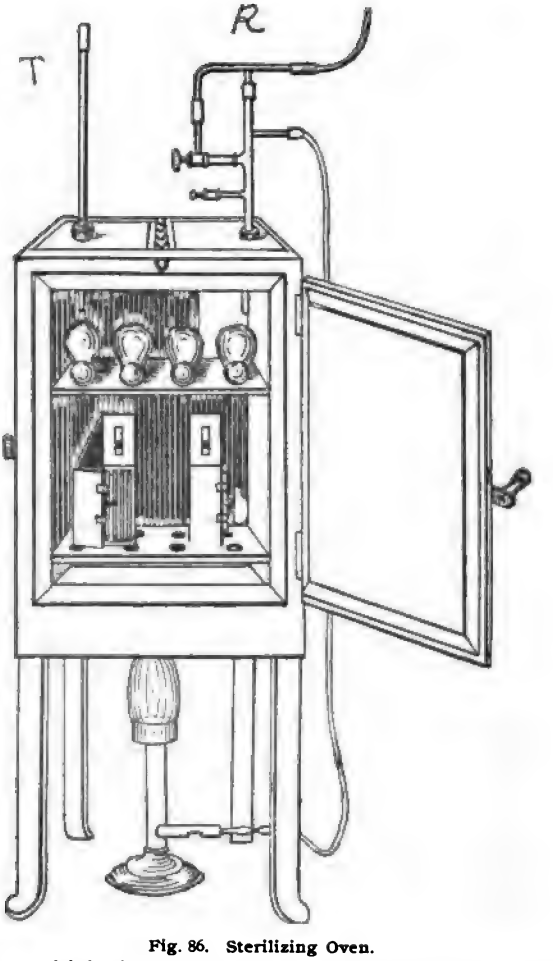

Fig. 86. Sterilizing Oven.

in vessels to which the steam can have access and then admitting steam from a boiler at any required pressure. In the case of small apparatus, such as the autoclave, the steam can be genera-

ted in the apparatus itself. The variety of apparatus used in the above method of sterilization is very great, but all the forms of apparatus employed depend upon the principles indicated.

506. The Sterilizing Oven.—The apparatus for sterilization by means of hot, dry air usually consists of a double-walled vessel made of sheet-iron, usually with a copper bottom. The apparatus is shown in Fig. 86.

The temperature is observed by means of a thermometer, T, and controlled by the gas-regulator, *R*. This is one of the ordinary gas-regulators by means of which the amount of gas supplied to the lamp is increased if the temperature should fall, and diminished if it should rise above the required degree. The best form of the sterilizing ovens is provided with a means for circulating the hot air so that the temperature may be made uniform throughout the mass. This can be accomplished by introducing a mechanical stirrer, or by the movement of the air itself.

Between the walls of the vessel may be placed water, provided the temperature of sterilization be not above that of boiling water. If it should require a higher temperature than boiling water, a solution of salt can be added until the required temperature is reached, or the space between the two walls may be left vacant and hot air made to circulate around the oven.

The exterior of the oven, except at the bottom where the lamp strikes the copper surface, should be protected by thick layers of asbestos or other non-conducting material. To avoid danger of flying filaments, this covering should be coated with some smooth paint which will leave an even surface not easily abraded.

507. Sterilization with Steam at High Pressure.—The apparatus used for this is commonly called an autoclave, and is shown in Fig. 87.

The top is movable and held in place by the clamp, *a*, which is held by the screw attached to the lever, *b*. The vessel itself is double-jacketed and the pressure is obtained from water in the vessel heated by means of the lamp, *c*. The actual steam pressure is indicated by the index *d*. The safety-valve, *e*, allows any excess of steam to escape above the amount required for the maintenance of the pressure. This, however, is best regulated by the lamp.

The outer jacket permits the heat from the lamp to circulate around the inner pressure vessel, and the holes near the top, *oo*, are for the escape of the heated gases. Enough water is placed in the bottom of the inner pressure vessel to supply all the aqueous vapor necessary to produce the required pressure and still leave some water in excess.

The materials to be sterilized are held on the shelves of the stand and the vessels may be of various kinds according to the nature of the material to be sterilized. The vessels containing the material being covered, the steam does not necessarily come in actual contact with it. At the end of the operation the safety-

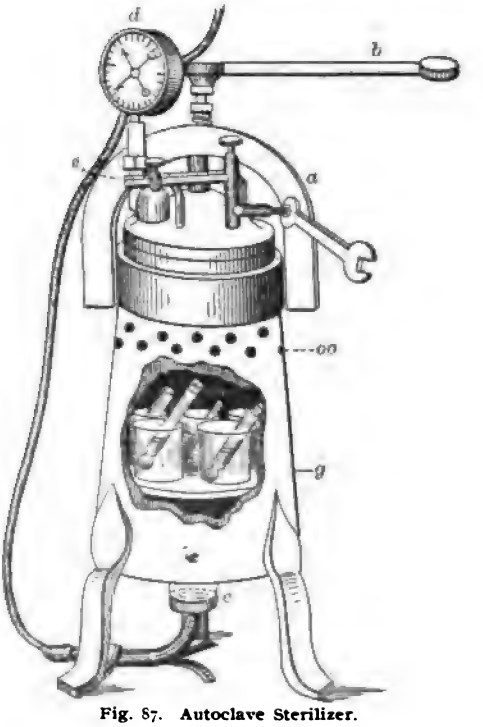

Fig. 87. Autoclave Sterilizer.

valve must not be opened to allow the escape of the steam, otherwise the remaining water would be rapidly converted into vapor and would be projected over the materials on the shelves. The lamp should be extinguished and the apparatus allowed to cool.

The autoclave is not only useful for sterilizing purposes but can be made of general use in the laboratory where heat under pressure, as in the estimation of starch, etc., is required.

These two forms of apparatus are sufficient to illustrate the general principles of sterilization by hot air and steam. There are, however, many variations of these forms designed for special use in certain kinds of work. For full descriptions of these, reference is made to catalogues of bacteriological apparatus.

508. Arnold's Sterilizing Apparatus.—A very simple and cheap steam sterilizer has been devised by Arnold.

Water is poured into the pan or reservoir, B, Fig. 88, whence

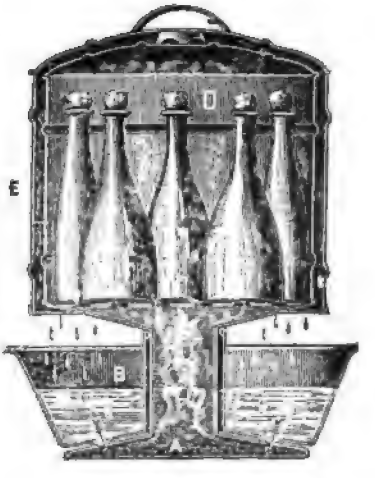

Fig. 88. Arnold's Sterilizer.

it passes through three small apertures into the shallow copper vessel, A. It is there converted into steam by being heated with any convenient lamp, and rises through the funnel in the center to the sterilizing chamber. Here it accumulates under moderate pressure at a temperature of 100°. The excess of steam escapes about the cover, becomes imprisoned under the hood, E, and serves to form a steam-jacket between the wall of the sterilizing chamber and the hood. As the steam is forced down from above and meets the air it condenses and drips back into the reservoir.

Such an apparatus as this is better suited to commercial purposes, as the sterilizing of milk, than for scientific uses.

509. Thermostats for Culture Apparatus.—It is important in the culture of micro-organisms that the temperature should be kept constant during the entire time of growth. Inasmuch as some operations continue for as much as three months or longer it is necessary to have special forms of apparatus by means of which

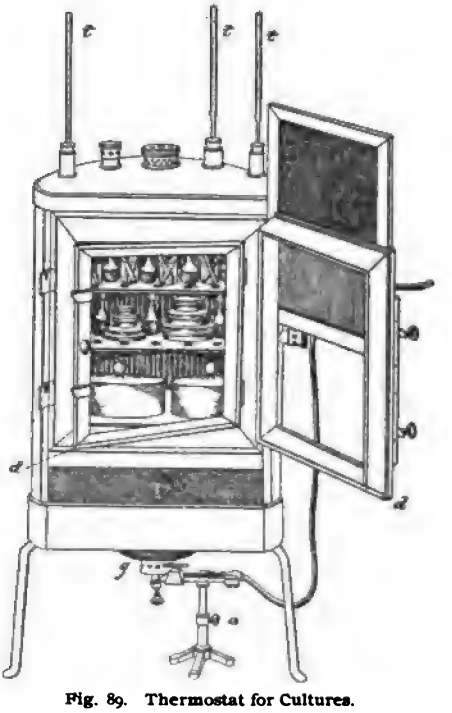

Fig. 89. Thermostat for Cultures.

a given temperature, during the time specified, can be maintained. This is secured by means of an oven with an automatic temperature regulator, practically built on the principle of the sterilizing autoclave, already described.

The essential principles of construction are, however, that the regulator for the temperature should be delicate and that the non-conducting medium surrounding the apparatus should be as perfect as possible, so that the variations in temperature from

changes in the exterior temperature, are reduced to a minimum. This delicacy is secured by introducing a drop of chloroform-ether into a confined space over the mercury of the regulating apparatus The doors of the chamber are double, the interior one being of glass so that the exterior door can be opened for inspection of the progress of the bacterial growth without materially interfering with the interior temperature. A convenient form is shown in Fig. 89.

The apparatus figured, is oval in shape, although circular or other forms are equally as effective. The arrangement of the lamp, *a*, thermometers, *t t t*, and gas-regulator, *g*, and the double doors, *d d*, is shown in the engraving and does not require further description.

The usual temperatures for cultures range from 22° to 35°, and the apparatus once set at any temperature will remain with extremely minute variations for an indefinite time. The apparatus possesses a heat zone which, by the arrangement of the regulator, is kept absolutely constant. The space between the walls of the apparatus being filled with water, the temperature is maintained even in every part. The apparatus, as constructed, is independent not only of the surrounding temperature within ordinary variations, but also of the pressure of the barometer. Three thermometers are employed to determine the temperature of the heating zone, the water space and the inner space. The arrangement of the gas-regulator is of an especial kind, as mentioned above, by means of which the consumption of gas is reduced to a minimum. This apparatus can be regulated to suit the character of the work.

510. Microscopic Apparatus Required.—Any good microscope, capable of accurate observation, of high power, may be used for the bacteriological observations necessary to soil analysis.

Preference should be given to the patterns adapted to receive any additional accessories which may be subsequently required for advanced work. The stage, in addition to being fitted with a sliding bar, should have a large circular or horseshoe opening to facilitate focusing operations. A mechanical stage is a desirable acquisition if really well made, but a plain stage is preferable for many purposes. A rackwork, centering sub-stage is essential for

advanced work, and in the absence of the more complete form, there should at least be a fitting beneath the stage to take the diaphragm and condenser. An iris diaphragm will be found more useful than any other kind in practice, since the size of the opening can be increased very gradually at will.

One of the best lamps is known as the paraffin lamp and is fitted with a half-inch wick. This will give even more light than is actually required, and a steady flame, perfectly under control, may be obtained. For the minute details to be observed in high-grade microscopic work, such as is required in the bacteriological examination of soils, reference must be had to the standard works on bacteriology and microscopy.

511. **General Conclusions.**—The nitrogenous food of plants is provided in several ways; *viz.*, (1) By the nitrogen brought to the soil in rain and snow. This nitrogen is chiefly in the form of ammonia and nitric acid. The nitrogen gas in solution in rain water has no significance as a plant food. (2) By the action of certain organisms herding in the rootlets of leguminous plants, free nitrogen may be oxidized and put into form for assimilation. (3) By the action of certain organisms on nitrogenous compounds pre-existing in the soil, ammonia, nitrous acid, and finally, nitric acid, are produced. It is believed that the plant organism, unaided by the activity of a micro-organism, is usually unable to assimilate nitrogen unless it be fully oxidized to nitric acid. (4) There exist micro-organisms capable of acting directly on free nitrogen independent of other plant growth, but the significance of this possble source of plant food is, at the present time, unknown. (5) The micro-organisms of importance to agriculture may be isolated and developed to the exclusion of other organisms of a similar character. This isolation is best accomplished in culture-media consisting essentially of a mineral gelatin to which is added only pure carbohydrates and the necessary mineral nourishment. (6) The nitrifying ferments consist probably of several species, of different geographic distribution. Different types of soil probably have nitrifying organisms of different properties. This is illustrated by the fact that nitrification is accomplished in dry alkaline soils under conditions in which the ordinary nitrifying

organisms would fail to develop. (7) The study of typical soils in respect of the kind, activity, and vigor of their nitrifying organisms has become as important a factor in soil analysis as the usual determination of physical and chemical composition.

DETERMINATION OF NITRIC AND NITROUS ACIDS IN SOILS.

512. Classification of Methods.—The minute quantities in which highly oxidized nitrogen exists in soils render the operations of its quantitative estimation extremely delicate. On the other hand, the easy solubility of these forms of combination and the absence of absorptive powers therefor, in the soil, render the separation of them from the soil a matter of great ease. It is possible, therefore, to secure all the nitrates and nitrites present in a large quantity of earth in a solution which can be concentrated under proper precautions to a volume convenient for manipulation. The method of this extraction is the same for all the processes of determination. The methods of analysis suited to soil extracts, as a rule, may also be used in the determination of the same compounds in rain, drainage, and sewage waters, and for the qualitative and quantitative control of the progress of nitrification. The various processes employed may be classified as follows:

1. The conversion of the nitrogen into the gaseous state and the determination of its volume directly. This is accomplished by combustion with copper oxid and metallic copper.

2. The conversion of the nitrogen into nitric oxid and the volumetric determination thereof. The decomposition of a nitrate with ferrous chlorid in the presence of free hydrochloric acid is an instance of this type of methods.

3. The oxidation of colored organic solutions and the consequent disappearance of the characteristic color, or its change into a different tint. The indigo and indigotin processes are examples of this method.

4. The production of color, in a colorless or practically colorless solution, by the treatment thereof with the nitrate in presence of an acid which decomposes it with the liberation of oxidizing compounds. The depth of color produced is compared with that formed by a known quantity of a pure nitrate solution until the

two colorations are alike. The methods depending on the use of carbazol or acid phenol sulfate illustrate this class of reactions.

5. The conversion of the nitrogen into ammonia by moist combustion with sulfuric acid in the presence of certain organic compounds, *e.g.*, salicylic acid, and the collection of the ammonia in standard acid, the excess of which is determined by titration.

6. The reduction of nitrates to ammonia by nascent hydrogen and the recovery of the ammonia produced by distillation and collection in standard acid.

7. The reduction of nitrates by electrolytic action and the collection of the ammonia as above.

8. The decomposition of nitrates with the quantitative evolution of a different element, and the direct or indirect measurement of the evolved substance. The quantitative evolution of chlorin on treating a nitrate with hydrochloric acid, the collection of the chlorin in potassium iodid, and the determination of the iodin set free, form a process belonging here.

513. **Relative Merit of Methods.**—The process mentioned in the classifications embraced under numbers (1) and (5) of the preceding schedule are sufficiently described in the paragraphs devoted thereto, under soil and fertilizers. In practice at the present time it is rare to determine the nitrogen in nitrates by the copper oxid method. The more rapid if not equally scientific processes of colorimetric comparison or reduction by nascent hydrogen are to be preferred when only small quantities are present.

The indigo methods among the colorimetric processes are not so much in use now as those which depend on the development of a color. Lawes and Gilbert considered them far inferior to the Schlösing method. The developed color methods are especially delicate and are to be preferred in all cases where the detection of the merest traces of nitrates is desired. Where nitrates are present in considerable quantities the reduction method with nascent hydrogen is to be preferred over all others. In all these cases the judgment of the analyst must be exercised. The particular method to be employed in any given case can not be determined save by the intelligent discrimination of the operator. Since these methods are also applicable to the determination of oxidized

nitrogen in fertilizers the detailed discussion of them will be given in volume second. Those peculiarly suited to determine the traces of nitrous and nitric acid in the small quantities produced in nitrification studies are given in previous paragraphs 474 and 475.

514. **The Extraction of Nitric Acid from the Soil.**—The easy solubility of nitric acid and of nitrates in water is taken advantage of in the separation of these bodies from the soil. A convenient quantity, usually about 1,000 grams of the fine soil, is used for the extraction. Instead of freeing the soil entirely from water, it is better to determine the amount of water in the air-dried or prepared sample, and base the calculation on 1,000 grams of the water-free soil.

All samples of soil for the purpose of examining for nitrates, should be rapidly dried to prevent the process of nitrification from continuing after the sample is secured. For this purpose the soil should be placed in a thin layer in a warm place, 50°-60°, until air-dried. It still contains in this case a little moisture but not enough to permit nitrification to go on.

One thousand grams of soil prepared as above are treated with 2,000 cubic centimeters of distilled water, free of nitric acid, and allowed to stand for 48 hours with frequent shaking. One thousand cubic centimeters of the extract are then filtered, corresponding to 500 grams of the dry soil. A small quantity of pure sodium carbonate should be added to the filtrate which is then evaporated on a water-bath to a volume of about 100 cubic centimeters. Should a precipitate be formed during evaporation it should be separated by filtration, the filter washed thoroughly, and the filtrate again evaporated to a volume of 100 cubic centimeters.

For the determination of nitrates, it is well to extend the sampling to a considerable depth. If the sampling extend only to the depth of nine inches, it should be in dry weather when the nitrates are near the surface.

The temperature at which a soil is dried has also an influence on the quality of nitric nitrogen remaining after desiccation.

If a wet soil be dried at 100°, the nitrates present will suffer partial decomposition. This is probably due to deoxidation by organic matter present. On the other hand, ordinary air-drying

affords opportunity for continued nitrification, thus increasing the residuum of oxidized nitrogen.

The method of drying practiced at Rothamsted, in order to secure results as nearly accurate as possible is the following:[73]

The soil is broken up directly after it is taken from the field, and spread on trays in layers one inch deep. The trays are then placed in a room at 55°. The drying is completed in 24 hours. After drying, stones and roots are removed, and the soil is finely powdered and placed in bottles.

For extracting the nitrates, a funnel is prepared by cutting off the bottom from a bottle four and a half inches in diameter. A nicely fitting disk of copper gauze is placed in the bottom of this funnel, and this is covered with two filter papers, the upper one having a slightly greater diameter than the lower. The paper is first moistened, and then from 200 to 500 grams of the dry powdered soil introduced. The funnel is connected with the receiving flask of a filter pump, and pure water poured on the soil until it is thoroughly saturated. The water is then added in small quantities. When the filtrate amounts to 100 cubic centimeters the process may be discontinued, since all the nitrates in the soil will be found in this part of the filtrate.

The extract obtained as above is evaporated to convenient bulk for the determination of nitric nitrogen.

[73] Journal of the Chemical Society (Trans.), 1882, **41** : 357.

PART EIGHTH

SPECIAL EXAMINATION OF WATERS, VEGETABLE SOILS, AND UNUSUAL SOIL CONSTITUENTS.

515. Further Examination of Waters.—Having described in the preceding part methods of determining the oxidized nitrogen in the products of nitrification where the quantity is very minute, there remains to be considered the examination of waters and soil extracts for other substances of importance to agriculture. Rain waters add practically nothing to the soil of value as a plant food but nitric acid and ammonia, and, therefore, demand no further discussion here. In drainage and sewage waters, in addition to the oxidized nitrogen, there may be sufficient quantities of phosphoric acid and potash to make their further analysis of interest. But by far the most practical point to be considered is in the case of waters used for irrigation purposes where the continued addition to the soil of mineral matters may eventually convert fertile fields into barren wastes. In irrigated lands where there is practically no drainage nearly the whole of the water is removed by superficial evaporation. It is easily seen in such a case how these mineral matters tend to accumulate in that part of the soil in which the rootlets of plants seek their nourishment.

516. Sampling Waters for Irrigation.—To secure a sample of irrigation water from a reservoir, which will represent the entire body of water, is a comparatively easy matter. The method followed in the Bureau of Chemistry is as follows: It is only necessary to get small and equal sub-samples from just below the surface, about half way down, and about two feet from the bottom of the reservoir, at several different points, and mix all the sub-samples thus obtained.

In the case of irrigation waters from streams the following procedure is followed in securing a sample which will represent the stream at any particular time:

Small and equal sub-samples are obtained at the surface half way down, and about two feet from the bottom, at a number of points equidistant from each other and transverse to the stream.

All of the samples are mixed and an aliquot part represents the daily sample.

If the true value of a stream for irrigation purposes is desired, even this single sample is valueless. The only method of attacking such a question as this is to mix equal daily samples secured as above in weekly periods and subject the weekly samples to a chemical examination. Even this method is applicable only so long as the stream has a fairly constant flow. In floods periods or when the character of the water evidently changes materially, a new composite should be started, and sampling continued daily as long as the flood continues. If this flood period extends over more than one week, more than one composite is necessary.

517. **Estimation of Total Solid Matter.**—The total solid contents of a sample of water are determined by evaporating a known quantity to dryness and weighing the residue. For comparative purposes a given volume of water, measured at a temperature of about 15°.5, may be used if the solid contents do not exceed four grams in a United States gallon, and each cubic centimeter then represents a weight of one gram. Where the content of mineral matter is greater it is best to weigh the water and calculate the solid contents to parts per one hundred thousand or million. Formerly it was customary in the United States to state the content of solid matter in grains per gallon. Since, however, the gallon has so many different values it is always necessary to indicate what particular measure is meant.

In ordinary spring and well waters a convenient volume is 100 cubic centimeters. To avoid calculation a volume in cubic centimeters corresponding to some decimal part of a gallon in grains is employed and the weight in milligrams will then be equivalent to grains per gallon. Thus in the imperial gallon which contains 70,000 grains of distilled water at 15°.5 if the residue after evaporating 70 cubic centimeters weigh 25 milligrams the water contains 25 grains of solid matter per gallon. The United States gallon at 15°.5 contains 58,304 grains of distilled water. In this case 58.3 cubic centimeters should be used, or double this amount and the weight in milligrams be divided by two.

The evaporation may be made in a platinum, porcelain, or

aluminum dish, preferably with a flat bottom. The dish does not need to hold the whole volume at once, but the water may be added from time to time as the evaporation continues. The dish, however, should, as a rule, hold not less than 100 cubic centimeters. The evaporation is best conducted over a steam-bath, and after the complete disappearance of the liquid the heating should be continued until the residue is perfectly dry.

In the case of mineral waters highly impregnated with inorganic salts, a smaller volume or weight is advisable, and greater care must be exercised in drying the residue. For the purpose of determining the percentages of special ingredients, quantities of the water inversely corresponding to the content of the ingredients desired are used. In general, for this purpose, it will not be necessary to evaporate the sample to complete dryness, but only to concentrate it to a volume convenient for the application of the analytical process. Where a complete quantitative analysis of the solid residue is desired, a sufficient quantity of the water is evaporated to give a weighable amount of the least abundant ingredients. The total solid content of the water having been previously determined, the actual weight or volume of the water evaporated to obtain the above residue is of no importance in so far as calculations are concerned.

518. Estimation of the Chlorin.—The chlorin in the solid residue from a sample of water may be determined directly by dissolving the soluble salts in distilled water, to which enough nitric acid is added to keep the solution slightly acid. After filtering and washing, silver nitrate is added, little by little, with constant shaking until a further addition of the reagent produces no further precipitate. The beaker or flask is placed in a dark place, on a shaking apparatus which is kept in motion until the precipitate has entirely settled in a granular state. The silver chlorid is collected on a gooch, washed free of all soluble matter, dried at 150°, and weighed. If the precipitate be ignited to incipient fusion, a porcelain gooch should be used.

A more convenient method is to determine the chlorin directly in the water, or, where the quantity is too minute, after proper concentration, volumetrically by means of a titrated solution of silver nitrate, using potassium chromate as indicator. As soon as

the chlorin has all united with the silver, any additional quantity of the silver nitrate will form red silver chromate, the permanent appearance of which indicates the end of the reaction. This process is especially applicable to water, which in a neutral state contains no other acids capable of precipitating silver. The chromate indicator is not applicable in an acid solution.

519. **Solutions Employed.**—A quantity of pure silver nitrate, about five grams, is dissolved in pure water and made up to a volume of one liter. For determining the actual strength of the solution, 0.824 gram of pure sodium chlorid is dissolved in water and the volume made up to half a liter. Twenty-five cubic centimeters of this solution are placed in a porcelain dish, and a few drops of the solution of potassium chromate added. The silver nitrate solution is allowed to flow into the porcelain dish from a burette graduated to tenths of a cubic centimeter. The red color produced as each drop falls, disappears on stirring as long as there is any undecomposed chlorid. Finally a point is reached when the red color becomes permanent, a single drop in excess of the silver nitrate being sufficient to import a faint red tint to the contents of the dish.

The solution of pure potassium chromate is prepared by dissolving five grams of the salt in 100 cubic centimeters of water. Water with any considerable quantity of chlorin can be treated directly with the reagents, but when the percentage of chlorin is low, previous concentration to a convenient volume is advisable.

In waters containing bromids and iodids these halogens would be included with the chlorin estimated as above. For agricultural purposes such waters have little importance. In the case of soluble carbonates capable of precipitating silver this action can be prevented by acidifying the water with nitric acid and afterwards removing the excess of acid with precipitated calcium carbonate. In this reaction McElroy recommends the use of Congo paper, which is not affected by the carbon dioxid but is turned blue as soon as an excess of nitric acid is added. After the addition of the calcium carbonate the mixture should be boiled to expel carbon dioxid.[74]

[74] Bulletin No. 13, Division of Chemistry, Part 8 : 1021.

Irrigation waters from ordinary sources or derived from sewage rarely contain enough chlorin to make their use objectionable. On the other hand, when water is obtained for this purpose from near the sea or from artesian wells or from some rivers or streams, especially in time of drought, it may often contain a quantity of chlorin which will eventually do more harm to the arable soil than the water will do good.

520. Carbon Dioxid.—Free carbon dioxid in water has no significance in respect of its use for irrigation purposes. Such waters, however, are usually of a highly mineral nature and thus are justly open to suspicion when used for farm animals and on the field. The presence of free carbon dioxid as has already been pointed out in paragraph **42**, gives to water, one of its chief sources of power as an agent for dissolving rocks and ultimately forming soil. The estimation of the total free carbon dioxid in a sample of water issuing from a spring or well is a matter of some delicacy by reason of the tendency of this gas to escape as soon as the water reaches the open air and is relieved from the natural pressure to which it has been subjected. The actual quantity at the time of exit from the earth can only be determined on the spot and with many precautions. The actual quantity of the gas remaining in solution at any given time is determined as follows: One hundred cubic centimeters of the water are placed in a flask with three cubic centimeters of a saturated solution of calcium and two of ammonium chlorid. To this mixture are added 45 cubic centimeters of a titrated solution of calcium hydroxid. The flask is stoppered, well-shaken, and set aside for 12 hours to allow the complete separation of the calcium carbonate formed.

When the supernatant liquid is perfectly clear an aliquot part thereof, from 50 to 100 cubic centimeters, is removed, and titrated with decinormal acid, using phenacetin or lacmoid as an indicator. From the quantity of calcium hydroxid remaining unprecipitated the amount which has been converted into carbonate is calculated. The weight of carbon dioxid fixed as carbonate is determined by multiplying the number representing the weight of uncombined calcium hydroxid by 0.0022.

521. Examination of Irrigation Waters.—In the method follow-

ed by Haywood in the Bureau of Chemistry for examining irrigation waters the constituents usually determined are: the sulfuric acid ion, the carbonic and bicarbonic acid ions, chlorin, iron, aluminum, calcium, magnesium, sodium and black alkali, and sometimes silica, potassium and the nitric acid ion.

The acid and basic ions are determined by the methods in ordinary use, except that the combined sodium and potassium are weighed as sulfates instead of chlorids and the potash is then determined by the Lindo-Gladding method, described in volume second.

Black Alkali.—Black alkali is determined as follows:

The solutions required are:

Standard sodium carbonate $^1/_{25}$ normal.
Standard sulfuric acid $^1/_{25}$ normal.
Chloroform.
Erythrosin indicator:—0.25 grams of erythrosin dissolved in one liter of water.

Manipulation.—Two hundred cubic centimeters of water are placed in a platinum or silver dish and 50 cubic centimeters of the $N/_{25}$ sodium carbonate added. The contents of the dish are evaporated on the water- or steam-bath to complete dryness. The residue is rubbed up with distilled water free from CO_2 and transferred to a 100 cubic centimeter flask, made up to the mark, thoroughly shaken, and allowed to stand until the insoluble matter has completely settled. Fifty cubic centimeters of the clear supernatant liquid are transferred to a glass stoppered bottle of 200 or 250 cubic centimeters capacity. The bottle should be of the best white glass. Five cubic centimeters of chloroform and one cubic centimeter of the erythrosin are added and the solution titrated with $N/_{25}$ sulfuric acid. The 50 cubic centimeters aliquot represents 100 cubic centimeters of the orignial sample of water + 25 cubic centimeters $N/_{25}$ sodium carbonate. If less sulfuric acid is required for this titration than is necessary to balance the sodium carbonate added, part of the sodium carbonate has been used up by a reaction between some of the soluble salts of lime or magnesia and the sodium carbonate; *e. g.*, $CaSO_4 + Na^2CO^3 = CaCO^3 + Na_2SO_4$, in which case the water is said to be hard, and the hard-

ness expressed in terms of calcium sulfate or calcium carbonate, preferably the former. But if more than the equivalent amount of sulfuric acid is required than is necessary to balance the sodium carbonate added, then the sample is shown to have originally contained an excess of alkalinity, which it is customary to express in terms of sodium carbonate or "black alkali."

522. Determination of Carbonates and Bicarbonates.—The method used by Haywood in the water laboratory of the Bureau of Chemistry is the same as that of Cameron,[75] with a few added precautionary details. The following solutions are needed for the work:

(1) A $N/_{20}$ solution of potassium acid sulfate.

(2) Methyl orange and phenolphthalein solutions.

The method is as follows:

To 100 cubic centimeters of the water are added a few drops of phenolphthalein. When carbonates are present the usual red color will be evident. The solution is now treated with a $N/_{20}$ solution of potassium acid sulfate, adding the $KHSO_4$ at the rate of a drop every few seconds until the red color has completely disappeared. Towards the end of the reaction when the pink color becomes faint, the solution is stirred vigorously and a couple of drops of the $KHSO_4$ solution only added every minute. The reading on the burette is recorded and represents the conversion of carbonates into bicarbonates. One drop (not more) of methyl orange is now added which produces a pure yellow color. The titration with $KHSO_4$ solution is continued without refilling the burette until the faintest pink blush can be noted in the yellow solution. This is taken as the second end-point and the reading is made.

The first reading gives the amount of $N/_{20}$ $KHSO_4$ necessary to convert carbonates to bicarbonates and must be multiplied by .002979 to get the CO_3 ions present.

The second reading gives the number of cubic centimeters of $N/_{20}$ $KHSO_4$ necessary to convert the carbonates to bicarbonates plus the number of cubic centimeters necessary to act on the bi-

[75] American Chemical Journal, 1900, **23** : 471; 1906, **28** : 77.

carbonates formed in this reaction plus the number of cubic centimeters necessary to act on the bicarbonates already present in the solution. The number of cubic centimeters necessary to act on the bicarbonates already present is therefore found by subtracting twice the first reading from the total second reading. This multiplied by .003028 gives the grams of HCO_3 ions present.

Methods of Stating Results.—The results of analysis are stated in terms of parts per million of the various basic and acid ions present with the exception of silica, which is reported as such.

In combining the ions to form salts, the following procedure is used. If the "black alkali" figure is positive it is reported as sodium carbonate, if negative it is reported as calcium sulfate or calcium carbonate. The amounts of acid and basic ions corresponding to the black alkali are then subtracted from the total amounts of these constituents as found in the complete analysis. The residual basic and acid ions are then combined with each other in the following order: Ca, Mg, K, Na, to carbonic acid, bicarbonic acid, sulfuric acid and chlorin ions. Silica is reported as such and iron and alumina as the oxids.

523. **Other Constituents.**—The lime, magnesia, iron, alumina, potash, soda, sulfuric acid, nitric acid, chlorin, etc., are determined in the evaporated residue of large quantities of water by the methods in common use. In brackish water or mineral waters containing large quantities of common salt the chlorin may be estimated in solution without concentration.

524. **Extraction of Soil Water Unchanged.**—It is desirable to have a just conception of the composition of the aqueous content of the soil in a condition as nearly as possible that in which it actually exists. Schlösing has devised the following method of securing such a sample.[76] Soil which has just been taken from a field is placed in a powdered condition in a vertical cylinder and sprinkled lightly with an artificial rain of pure water. Divide the cylinder into very thin horizontal layers and suppose that the rain descends by parallel surfaces. The upper layer saturated with water yields to the next lower layer a first mixture of water and of solutions contained in the soil. The second will yield to the third a

[76] Comptes rendus, 1866, **63** : 1007.

mixture slightly richer and thus in regular order until a given layer will receive from the preceding one a solution of which the composition will be infinitely near that of the solution pre-existant. Beginning with this layer the portion of the solution contained in the layers lying under will be simply replaced and thrust finally without the containing vessel. Received by itself it becomes a sample representing in composition the moisture originally present in the soil.

A proof of the correctness of the theory is as follows: 1.2 kilograms of sand, washed and dried, was moistened with 200 cubic centimeters of a solution of common salt containing ten milligrams of chlorin per cubic centimeter. This was introduced into a vessel similar to the one described, covered with a roll of moist cotton for the purpose of distributing equally the pure water which was added at the rate of 40 cubic centimeters per hour. The liquid which was driven out was received in quantities of ten cubic centimeters. Each three quantities were placed together and the chlorin determined therefrom. The first three quantities contained 100.2 per cent, the second three 99.8 per cent, the third three 99.8 per cent, the fourth three 100 per cent, the fifth three 100 per cent, and from this point the quantity of chlorin rapidly diminished. The tenth three portions contained none. Thus it is seen that three-fourths, at least, of the solution in the sand was displaced without mixture with the added water. Other determinations were made to show that the solution which would be forced from a soil in a similar manner must correspond to that preexistant therein. In this way the normal and natural solutions in soils can be obtained in large quantities.

Applying the method to soils in a series of experimental research Schlösing reached the following conclusions: The first products received have a constant composition; these experiments bring into evidence effects to which little attention has been given, namely, the proportion of fertilizing principles carried off by the rain into the subsoil depends not only upon the quantity of water which falls, but also upon the state of humidity of the soil before the rain. For example, after a drought quantities of rain sufficient to saturate the soil and make infiltrations beyond the use-

ful portion of the soil will be able to cause more loss than a rain much less intense falling upon a soil already humid. Indeed, when there is placed in the presence of equal weights of soil solution, alkali solutions identical in composition but unequal in volume, the lot of soil placed in the presence of the largest volume will absorb much of the alkali; but when the solutions are displaced by water, solutions of alkaline salts are accumulated in the inferior layers. Although the alkaline solutions were at first impoverished by the absorption power of the soils, this did not prevent the establishment of a new equilibrium from which results the constance of the composition of the first liquid received.

Chevreul,[77] in discussing this theory, calls the attention of the Academy to the communication which he made on the 6th of June, 1853, recognizing the effect which a solid body insoluble in a liquid holding another body in solution is capable of producing upon that solution and that the method had pointed out three possible cases; first, where the solid matter takes more of the solvent than of the bodies dissolved; there is in that case a concentration of the solution. Second, the contrary case; third, finally the mean case where the solution after contact preserves its original state. The following experiments were made in connection with this: (1) Upon lime water placed in contact with glass, with sand, etc.; (2) Upon cotton, silk, and wool placed in contact with chlorid of sodium, with bichlorid of mercury, sulfuric acid, etc.

From the above it is seen that some of the general principles of physical chemistry were well recognized by Chevreul more than fifty years ago.

This method of displacing and obtaining the water content in the soils is well suited to the study of dissolved bodies in their natural state and has not received the attention its merits warrant. It permits operations to be carried on in the laboratory and under the most varied circumstances. Since its first publication Schlösing has sensibly improved it.[78] The displacement is secured from 30 to 35 kilograms of powdered soil in a large bell-jar as soon as possible after it is taken from the field. The artificial rain de-

[77] Comptes rendus, 1866, **63** : 1012.

[78] Comptes rendus, 1870, **70** : 98.

signed to replace the solution is distributed by a mechanism driven by a little hydraulic motor, which distributes the rain as gently as one could wish, for example, a half liter in 24 hours, and with such uniformity that the line of demarcation between the color of the earth saturated with water and that of the earth simply humid is maintained constantly in a horizontal plane during its descent, which may last three, four, or even eight days. The dispositions thus adopted permit of the analysis of the air confined in the earth, of the circulation therein of pure air or air charged with a given content of carbonic acid, and further permit the liquids to be received out of contact with the air in the laboratory and in an atmosphere the same as that of the original earth, a precaution which avoids the loss of carbonic acid and the consequent deposition of matters which this gas holds in solution.

Estimation of Carbon Dioxid.—The determination of the carbonic acid in the waters of the soil by this process is made twice by boiling. The first ebullition gives that which is free or combined as bicarbonates; the second ebullition after the addition of an acid gives that combined as neutral carbonates. Schlösing has shown that in a boiling liquor the dissolved silicic acid partially decomposes the carbonates of lime and of magnesia, from which it is inevitably certain that the first operation gives an excess of gas if it is too prolonged, or a loss if it is not prolonged enough. It is not surprising, therefore, if in such analyses there is not an absolute equality between the sum of the equivalents of the bases and that of the equivalents of the acids.

Quantities of Phosphoric Acid.—Further information concerning the composition of the solutions obtained from the soil gives the total phosphoric acid in conjunction with the iron, the largest amount of the two together in any one soil was 2.8 parts per million. Five of the samples contained no phosphoric acid and iron in the solutions. Only three out of the 18 samples had above one part per million.

It is thus seen that in the soil moisture which must be absolutely normal, the quantities of phosphoric acid even when augmented by the iron present are found to be extremely minute.

525. Quantity of Phosphoric Acid in Soil Water.—It is known

that the water existing in soil holds in solution a very small quantity of phosphoric acid. This quantity is embraced usually between a few hundredths of a milligram to one milligram per liter, some times reaching as much as two or three milligrams, and in the opinion of some authorities appears generally without importance for the nutrition of plants.[79] In fact, a hectare, comprising 3,000 tons of earth, having 15 per cent of water and one milligram of phosphoric acid per liter in this water, would contain in the dissolved state only .45 kilogram of phosphoric acid, a quantity relatively very small to the content of the crop.

It has also been generally admitted, since the classical experiments of Sachs and others, that the essential source of phosphorus for vegetables resides in the phosphates not dissolved in the soil, phosphates attacked by the acid juices of the roots and utilized strains too much the rôle of the phosphoric acid which is found in the waters of the soil in a state of solution. This question has already been examined by Joffre in regard to the action of superphosphates.[80] The process employed in the extraction of the soil water is founded on the process which displaces the soil water very slowly by water poured in a regular shower over the surface of the soil.[81] If 40 kilograms of soil are treated in this way under proper conditions this process furnishes generally at least one liter of the same solution as that which existed in the soil without sensible alteration.

In the solution thus obtained Schlösing determines the phosphoric acid according to the method outlined below. The method consists in the evaporation in a flask of one liter of the soil water, to which is added a little nitric acid to drive off any hydrochloric acid present. The process is finished by evaporating to dryness in a platinum capsule and incinerating to destroy organic matter. After the addition of a small quantity of nitrate of ammonia the capsule is heated to render the silica insoluble, taken up with acidulated water and filtered. In the filtered liquor reduced to a very small

[79] Comptes rendus, 1898, **127** : 236.
[80] Bulletin de la Société chimique, do Paris, 1895-98,[3], **18** : 698.
[81] Schlösing pére, Comptes rendus, 1870, **70** : 98.

volume, (from two to four cubic centimeters), phosphoric acid is precipitated by molybdate of ammonia and determined with the usual precautions. In ordinary cases the quantity of lime is not in sufficient proportion to interfere with the determination, but frequently solutions are encountered in which it is desirable to eliminate the sulfuric acid with a view of avoiding an excess of sulfate of lime. The determinations by means of the phosphomolybdate reagent can be made with great precision. In seven different soils in which 40 kilograms of each were treated according to the above method the quantities of phosphoric acid per million were as follows: 1.02, 1.19, 1.05, 1.04, .98, .09, and .12, respectively.

The phosphoric acid which is dissolved in a soil results from the equilibrium between chemical actions which are very complex, tending on the one hand to render the phosphoric acid insoluble, and on the other hand to make it pass into solution in such a way that if by some cause the proportion of phosphoric acid dissolved diminishes, a new quantity of acid enters into solution in order to establish the primitive quantity, and *vice versa*. By the play of the phenomena of equilibrium, the phosphoric acid is capable of renewing itself in the waters of the soil in proportion as the vegetation consumes it. Whence, in spite of its feeble proportion, it is no longer to be deemed altogether negligible for the alimentation of plants.

526. Quantity of Phosphoric Acid Necessary to Plant Growth.— It has been generally thought that the phosphoric acid contained in the solutions impregnating the soil cannot, on account of its being always present in minute proportion, be of any very great utility and is almost negligible for vegetation. The younger Schlösing, on the contrary, has been led to think that, in spite of its rarity, it should be taken into serious consideration as a source of phosphorus for plants.[82] This rarity, indeed, is only in appearance, because phosphoric acid is able to renew itself in the solutions of the soil in proportion as the roots cause it to disappear. This renewal results in an equilibrium which without cessation tends to be established between the water and the almost in-

[82] Comptes rendus, 1898, **127** : 820.

finitely little soluble phosphates of the soil. This equilibrium is established also with a tolerably great activity in a soil which is gently shaken with water. It is accomplished, as has been shown, in a few hours, in such a way that during the course of a season of vegetation it is capable of furnishing to plants a good part of the phosphoric acid which they absorb.

It might be useful to push the demonstration further and to prove not only that the solutions of the soil can offer to plants an important quantity of phosphoric acid, but also that the plants can really secure their food exclusively or in a major part from the phosphoric acid present in a state of solution and in the very small doses which are met with in the waters of the soil.

Although many experiments have been made on the utilization of phosphoric acid by plants it does not appear that one has been made under the conditions in which by a gradual reduction of the phosphoric acid supplied in the water the limit of growth and development was determined. To ascertain this point, maize, beans, and wheat were cultivated on sterile soils, irrigated with nutritive solutions in which the phosphoric acid in a soluble state varied from nothing to two milligrams per liter, that is, two parts per million. These experiments show that when the amount of phosphoric acid reaches two milligrams per liter plants are produced of full growth, while when the amount of phosphoric acid is reduced to less than one-tenth milligram per liter the plants are dwarfed and only slightly developed. When sterile soils unsuited by themselves to properly feed plants with phosphoric acid are irrigated with nutritive liquids containing this acid in different proportions, plants have been able to take phosphoric acid almost exclusively from the solutions of it which was offered them. Without the addition of phosphoric acid in these solutions the plants remained undeveloped. In presence of the solutions containing the quantities of phosphoric acid in the order in which they exist in arable soils they have prospered. With solutions containing two milligrams of phosphoric acid per liter there was obtained a very good crop of maize, and with solutions which contained one-half milligram and one milligram, respectively, the harvests of wheat corresponded to ten and 18 hectoliters per hectare, respectively.

527. Colorimetric Estimation of Phosphoric Acid.—It has been shown that in soil waters only minute traces of phosphoric acid are usually found. Attempts have been made to determine such traces, often too small for gravimetric treatment, colorimetrically. The methods proposed for this purpose have been reviewed by Veitch.[83] The methods of Lepiere[84] and of Woodman any Cayvan[85] promised the most valuable results.

The chief difficulty in the process is due to the necessity of removing from the solution all matters except phosphoric acid, which affect the color of the solution. Among these silica is the most active, but organic matter, aluminum sulfate and iron have much interfering power. All suspended matter is first removed by filtering through paper or through porcelain and organic matter is then destroyed, which is best accomplished by ignition with magnesium nitrate and subsequent evaporation with nitric acid. Traces of silica in equivalent proportions have about 1.8 times more power to form color with an ammonium molybdate solution than phosphoric acid. Its entire removal is, therefore, a condition of even approximately accurate results. Schreiner[86] having observed that silica solutions give different intensities of coloration under different conditions, uses this fact as the basis for the estimation of both silica and phosphoric acid without removal of the silica. In the solution are found in a given case silica and phosphoric acid. Under certain conditions silica gives a color reading only half as great as that given under another condition, but phosphates always give the same color. The results are calculated from the following formulæ

$$(1) \quad x + y = a$$
$$(2) \quad \tfrac{1}{2}x + y = b$$

where x equals silica, y equals phosphoric acid, "a" equals the reading under one condition and "b" equals the reading under the other condition.

Determination of the "a" *Reading.*—To 50 cubic centimeters of the solution add five cubic centimeters of nitric acid reagent and

[83] Journal of the American Chemical Society, 1903, **25** : 169.
[84] Bulletin Société Chimique de Paris, 1896, [3], **15** : 1213.
[85] Journal of the American Chemical Society, 1901, **23** : 96.
[86] Journal of the American Chemical Society, 1903, **25** : 1056.

four cubic centimeters of ammonium molybdate reagent, and after 20 minutes the color reading is made.

Determination of the "b" *Reading.*—To a second portion of 50 cubic centimeters of the solution add four cubic centimeters of ammonium molybdate solution and allow to stand one hour, then add five cubic centimeters of nitric acid reagent making the readings and the values of phosphoric acid and silica readily calculated. The silica reading is twice the difference between the "a" and "b" readings. The silica reading multiplied by .00525 equals milligrams of silica and the phosphoric acid reading multiplied by .01 equals milligrams of P_2O_5.

The accuracy of the method has been confirmed by Lincoln and Barker.[87]

In pure colorless solutions the colorimetric method as conducted by Veitch gives results fairly concordant with the official gravimetric and volumetric determinations. The attempt to apply colorimetric methods to soil extracts directly may lead to grave errors even in experienced hands and to avoid this all the precautions mentioned should be observed. The use of more concentrated extracts carefully freed of interfering bodies is therefore to be advised and these are conveniently obtained by evaporating a large volume of the extract.

As is well observed by Veitch, the method is so delicate and it has been shown there are so many points at which errors may be introduced that the following precautions must be observed if anything like accuracy is to be reached.

The sodium phosphate ($Na_2HPO_4 + 12H_2O$) from which the standard is made must be practically pure, and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxid per liter, and then dilute this to ten parts per liter for the reading standard. The greatest care should be used in making this standard as it is here where errors count. Ten cubic centimeters of the 100 parts per liter solution should be run into a standardized 100 cubic centimeter flask from an accurately graduated burette. Dilute to about 80 cc. at 20°-25° with distilled water (free from SiO_2 and P_2O_5), add ten cubic centi-

[87] Journal of the American Chemical Society, 1904, **26** : 975.

meters of nitric acid (1.07) and eight cubic centimeters of ammonium molybdate complete to volume and mix thoroughly. This is the standard with which the unknown solutions are to be compared and it should be made fresh each day.

All reagents including distilled water must be kept in Jena glassware, tested from time to time and made fresh when a mixture of them shows color after standing some time.

As the colorimetric tubes may have a slight color themselves, each should be tested and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a one part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron.

A correction must be established for each package of filter-paper used. This correction is small, but is not to be neglected.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

The working errors may only be neglected when at least 200 cubic centimeters are taken for the determination.

REAGENTS FOR THE COLORIMETRIC DETERMINATIONS OF PHOSPHORIC ACID.

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in one liter of solution.

(2) *Nitric Acid* (sp. gr. 1.07).

(3) *Standard Phosphate Solution.*—0.5045 gram of pure freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in water, 100 cubic centimeters of nitric acid (sp. gr. 1.07) added, and the whole diluted to one liter. The nitric acid is added to lessen the contamination with silica from the glass. One cubic centimeter = 0.0001 gram P_2O_5.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting ten cubic centimeters of the above standard phosphate solution to about 80 cubic centimeters and then adding nine cubic centimeters of nitric acid (sp. gr. 1.07), and eight cubic centimeters of ammonium molybdate reagent and making up to 100 cubic

centimeters. After standing 20 minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 grams P_2O_5.

528. Colorimeter for Phosphoric Acid Determination.—The colorimeter shown in the accompanying illustration consists essentially of graduated glass tubes containing the standard and the unknown colorimetric solution, the length of the column of liquid in both tubes being changed by means of two smaller immersion tubes, also of glass.[88] The immersion tubes (A), which are 26 centimeters in length and about two centimeters in diameter, resemble the narrow Nessler tubes, the bottom being well ground and polished. The upper ends of the tubes are mounted in blocks of wood which fit into grooves on the body of the colorimeter as shown. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes (B) have well ground bottoms and are likewise 26 centimeters in length, but have a diameter of about three centimeters. The scale divisions are two millimeters apart. On the reverse side of the tube there is a 50 cubic centimeter and a 100 cubic centimeter mark for making the solutions up to definite volume. These tubes are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps (C), the tension of which can be regulated to suit the diameter of the tube, so as to allow it to be freely moved up or down by hand and yet be firmly held in position when the setting is made. It will be noticed from the figure that the glass tubes diverge slightly. This has been found of advantage, as it allows the operator to look down the center of both immersion tubes, as well as to bring the upper parts of the tubes, and consequently the images, closer together.

The tubes are illuminated from the reflector (D), which carries a white sheet of cardboard or opal glass, and after passing through the tubes the light is reflected by a mirror (E) in the upper part of the instrument to the eye of the observer at (F). The dimensions of the camera are about 70x32x16 centimeters.

To make the comparison the standard colorimetric solution is

[88] Journal American Chemical Society, 1905, 27 : 1192.

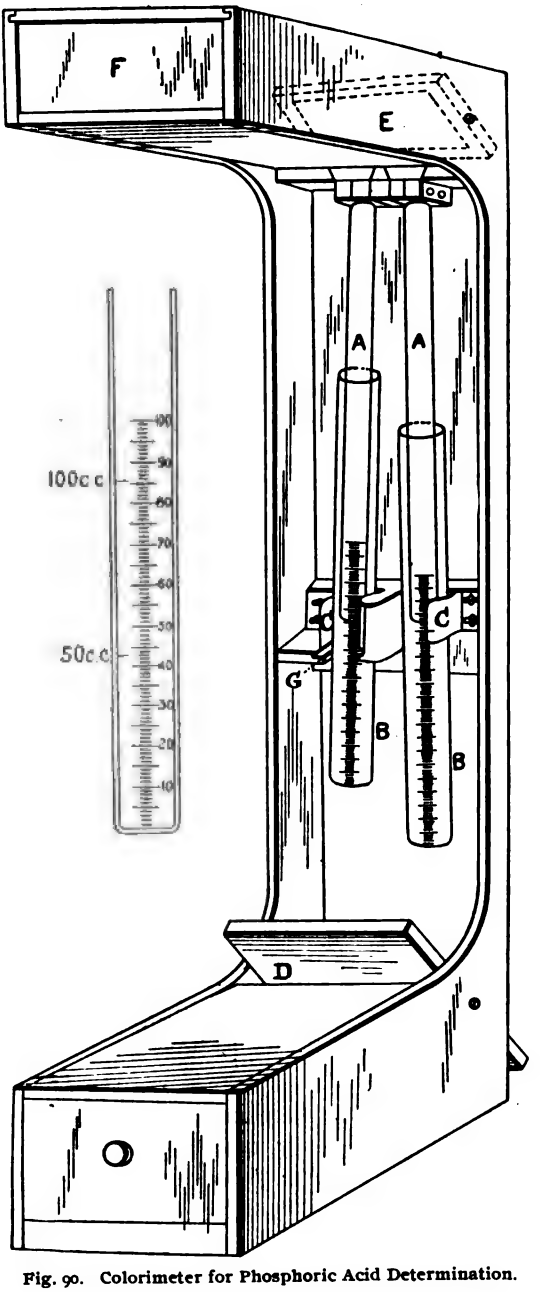

Fig. 90. Colorimeter for Phosphoric Acid Determination.

poured into one of the graduated tubes and put into place with the immersion tube, as shown in the figure. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the standard is set at a convenient height and the other tube containing the liquid of unknown strength, moved up or down, the operator watching the effect on the images in the mirror through the opening (F). By moving the tube so that the image is alternately weaker or stronger than the standard, the setting can be accurately and quickly made. When both images show the same intensity of color, the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the unknown solution which exactly corresponds with the intensity of color of the column of the standard solution. It follows, that the strengths of these two colorimetric solutions are inversely as the heights of the columns; that is, as the readings on the two tubes. If R is the reading of the standard solution of strength S, and r the reading of the colorimetric solution of unknown strengths s, then

$$s = \frac{R}{r} S$$

The same formula, of course, applies when the unknown solution is fixed and the standard moved up or down until the images are of equal intensity. Standard glass slides may be inserted at (G) in place of the tube containing the standard solution. The tube (A) is, however, retained so as to give similar images when viewed from above.

529. Colorimeter of King and Whitson.—Another instrument used prior to the one just described is that of King and Whitson.[89] It consists of a tube of colorless glass, one inch by ten inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution;

[89] University of Wisconsin Agricultural Experiment Station, Bulletin No. 85 : 38.

a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cubic centimeter and 100 cubic centimeter mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cubic centimeter mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

The water or extract is tested for iron by adding potassium ferrocyanid to the acidified solution. The absence of interfering accounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a porcelain filter (reject the first 100 cubic centimeters that pass) or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or color is corrected for by determining its amount in terms of the standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract five cubic centimeters of nitric acid (sp. gr. 1.07) and four cubic centimeters of molybdate solution. Place in the camera, allow 20 minutes for development of color and compare with a standard phosphate solution, which may conveniently contain ten parts per million of phosphorus pentoxid. The color of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh every day. The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 cubic centimeters, equals $P_2O_5 + SiO_2$ in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice (with a filtration between the evaporations) in a porcelain or platinum dish with three cubic centimeters of nitric acid (sp. gr. 1.07) and with a little magnesium nitrate, heated two hours in a water oven, five cubic centimeters of nitric acid

(sp. gr. 1.07) added, filtered, washed to about 45 cubic centimeters, placed in a camera and compared.[90]

If colored, the reading is noted, and is finally subtracted from the total reading. Add four cubic centimeters of ammonium molybdate and thoroughly mix. Place in the camera and compare after five minutes. The corrected reading calculated to a volume of 100 cubic centimeters is P_2O_5 in parts per million of solution. This reading subtracted from the $SiO_2 + P_2O_5$ reading and the difference multiplied by 0.55 gives the silica.

Where lime and magnesia salts are absent a single evaporation to dryness will usually remove all the silica while, in the presence of these salts two or more evaporations are required.

Where the original solution is too much colored with organic matter to be accurately corrected for by reading the color thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gram magnesium nitrate[91] and burn off the organic matter, take up with water to which three cubic centimeters of the nitric acid reagent have been added, evaporate to dryness and heat two hours in the water oven. Add five cubic centimeters of nitric acid and proceed as above. In this case silica is not determined.[92]

SPECIAL TREATMENT OF PEAT SOILS.

529½. **General Considerations.**—Deposits of peat which are to be used as soil for cultural purposes, or marsh lands, containing large quantities of organic matter, require a special treatment in addition to the general principles of examination illustrated in the previous pages. These soils, essentially of an organic origin, do not permit of the same treatment either chemical or physical as is practiced with soils of a mineral nature. For instance, it would

[90] Or the procedure of Schreiner given above may be used.

[91] In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

[92] Or the organic matter may be destroyed by treating with aqua regia n the presence of sufficient base to prevent loss of phosphoric acid.

be useless to attempt a silt analysis with organic soils, and the extraction of them with hydrochloric acid for the purpose of determining the materials passing into solution would prove of little utility. The object of the examination is not only to obtain knowledge of the ultimate constituent of the sample, but also, and this is the practical point, to gain some idea of the stores of plant food in the soil and of the proper steps neccessary to secure a supply of the deficient nutrients. The final analytical processes for the estimation of the constituents of a peat or vegetable soil are the same as those already given, but the preliminary treatment is radically different.

530. **Sampling.**—First of all the geological and meteorological conditions of the peat formations must be determined as nearly as possible. It is fair to presume that these formations are of comparatively recent origin, in fact that they are still in progress of evolution. The geological formation in the vicinity of the deposit should be noted. Information should be obtained in respect to the character of the water, whether running or stagnant, fresh, salt, or brackish, and the changes of level to which it is subject, should be noted. It should be particularly stated whether the vegetable growth contributing to the formation be subject to frost or freezing. The character of the growth is to be carefully noted, and observation made of any changes in vegetation due to drainage preparatory to cultivation. It is to the original vegetation that the chief vegetable accretions in the peat must be accredited. In all cases, for purposes of comparison, some samples must be secured from parts of the field which have not been under cultivation or fertilization. The original properties of the peat can thus be determined and compared with the portions which have been changed under cultivation. If the vegetation in different parts of the field vary it is an indication that the peat is not homogeneous in structure and in such cases all the different kinds must be separately sampled. Any alluvial deposit should be carefully separated from the peat found *in situ*, for the two layers are radically different in nature.

The sampling should be made by digging a pit, if possible to the bottom of the peat formation, and getting the samples at

depths of one foot from one or all of the sides. The samples from sections of even depth are to be mixed and about five kilograms of the well-mixed sample preserved. Blocks of the unbroken and unshattered material should also be taken from each section for the purpose of determining permeability to water and air. All living vegetable matter should be as fully as possible removed before the sampling begins. The nature of the subsoil must be observed, and it should be stated whether it be sand, clay, limestone, etc. Fresh samples should be secured at various depths for the purpose of determining the content of moisture in the manner described in paragraph 75. The tubes used are made sharp at the end to be inserted in the soil, and so arranged as to cut cylinders of soil a trifle smaller than their interior diameter. By this means the sample slips easily into its place. The same care and judgment must be used in securing these samples as are required in the case of common soils.

Illustration.—Samples of peat soil from Runnymede, Florida.

(*a*) *Formation.*—Littoral fresh-water lacustrine deposits, varying from a few inches to four feet in depth, and from a few feet to half a mile in width.

(*b*) *Vegetation before drainage.*—Saw grass (*Cladium Mariscus or* effusum).

(*c*) *Principal present vegetation.*—(See pages 49-50).

(*d*) *Kinds of Soil.*—The peat shows two distinct colors, black and brown. The vegetation, however, seems to be the same in both cases. The black peat has the appearance of being more thoroughly decomposed.

(*e*) *Geological Formation.*—This portion of the Florida peninsula is covered generally with sand due to marine submergence during recent geological periods. The forest growth is pine. The drainage from the pine land is towards the peat deposits. The pine land lies from four to ten feet higher than the surface of the peat and is much less subject to frost.

531. **Water Content.**—The capacity of a peat soil for retaining water is very great. In a moist state these soils are heavy and apparently quite firm. When dry they are light and fluffy and unsuited to hold the rootlets of plants. Saturated to their great-

est capacity they hold considerably more than their own weight of water. Attention has already been called to the danger of drying such samples at a high temperature. As in most cases of drying exposure at the temperature of boiling water until a constant weight is obtained is a perfectly safe way. It is hard to say what comes off in addition to water at a higher temperature. All that comes off even at the temperature of boiling water is not water.

The method of determination of water usually employed in the laboratory of the Bureau of Chemistry is the following:

From four to five grams of the material are spread as evenly as possible over the flat bottom of a circular aluminum dish, about seven centimeters in diameter. The dish is exposed for three hours at the temperature of boiling water and then kept for two hours in an air-bath at 110°. At the end of this time constant weight is obtained. Additional drying at 110° for five hours, usually gives no further loss of volatile matter. The dish should be covered during weighing on account of the hygroscopicity of the residue. When well sampled the dry matter thus obtained serves as the basis of calculation for the general analytical data.

Results.—Samples of peat soil placed in brass tubes in March during the dry season had the following contents of moisture:

	Matter volatile at 110°. Per cent.
From near the surface	61.60
" one foot below the surface	84.35
" two feet " " "	81.52

It is thus seen that the normal content of moisture in such a soil during the dry season, exclusive of the top layer, is about 80 per cent.

The drying of turf, peat or vegetable mold is best conducted in a partial vacuum whereby the action of oxygen on organic matter is excluded. It is well to keep the vessel in which the drying takes place free of all moisture by placing in it a dish of calcium chlorid or phosphoric anhydrid. The desiccator in which the sample is cooled before weighing should contain calcium chlorid or phosphoric anhydrid and not sulfuric acid.[98]

[98] Landwirtschaftlichen Versuchs-Stationen, 1895, **46** : 221.

532. **Organic Carbon and Hydrogen.**—The organic carbon and hydrogen in peat soils are determined on the carefully dried sample by combustion with copper oxid. This process gives not only the quantities of these bodies combined as humus, but also those in a less advanced state of decomposition and present as fatty bodies or resins. The method employed is given on pages 345 and following.

Results.—The data obtained on a sample of peat soil from Florida are as follows:

	Per cent. carbon	Per cent. hydrogen
One foot from surface.....	57.67	4.48
Two feet " "	47.07	5.15
Three " " "	8.52	0.53

The last sample was largely mixed with sand, the peat at the point where it was obtained not being quite three feet deep.

533. **Total Volatile and Organic Matter and Ash.**—The ignition of the sample should be very carefully conducted at the lowest possible temperature. About five grams of the air-dried sample or double that amount of the moist sample will be found to be convenient amounts. In the latter case the calculations should be made on the basis of the dry material. The ignition is continued with frequent stirring with a platinum wire until all organic matter is destroyed. At the same time in a large dish one or more kilograms of the sample is ignited in order to secure an ash for analysis. The ash is quickly weighed to avoid absorption of moisture.

534. **Sulfur as Pyrite.**—The sulfur present in peat is usually combined either in an organic form or with iron. It may be estimated by the method of Fleischer.[94]

An aqueous extract is made of the sample to be tested and examined for the presence of ferrous oxid by adding a solution of red ferricyanate of potash (Blutlaugensalz) thereto. The presence of iron in the ferrous state is revealed by the blue color produced. Any acid reaction is detected by means of litmus. In the aqueous extract of 100 grams of the peat, potash, soda, lime, magnesia, ferrous and ferric iron, chlorin and sulfuric acid are determined

[94] Wahnschaffe, Anleitung zur Wissenschaftlichen Bodenuntersuchung, 1093, 2nd edition, 147.

and the probable state of combination calculated. Any excess of sulfuric acid is regarded as having been present in a free state.

Twenty grams of the extracted and dried sample are ignited in a hard glass tube in a stream of air or better of oxygen. The sulfur existing as pyrites is converted into sulfuric or sulfurous acid.

The combustion is carried on in the apparatus shown in Fig. 91.

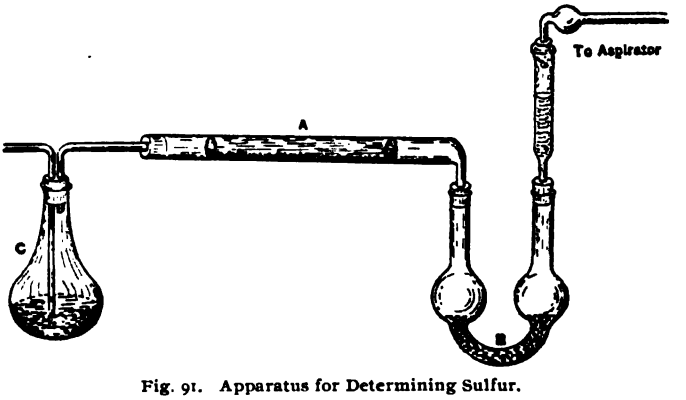

Fig. 91. Apparatus for Determining Sulfur.

The end of the tube A, next to B, is lightly stopped with a plug of glass wool, the substance introduced and held in place by a second plug of glass wool next to C. A is connected to the flask C, containing water, as is shown in the illustration. The chief object of the flask is to control the rate of aspiration of the air or oxygen. A is also connected with the bulb-tube B, as shown in the figure. B contains potash lye, free of sulfur. On the arm of B leading to the aspirator is placed a drying tube filled with glass pearls, moistened with potash lye. This is connected with the aspirator by a small bulb-tube bent at right angles, as indicated. The bulb of this tube contains a little neutral litmus solution, which must suffer no change of color during the progress of the analysis.

The tube, thus arranged, is placed in a combustion furnace and gradually heated to redness, beginning with the part next to B. A moderate stream of air or oxygen is passed through the tube by aspiration during the operation. Any product of the combustion collecting in the tube before reaching B, is driven into B by

careful heating. At the end of the combustion the contents of B are acidified with hydrochloric acid, and treated with bromin to convert the sulfurous into sulfuric acid. The excess of bromin is afterwards removed by boiling, and the sulfuric acid precipitated by barium chlorid and estimated in the usual way.

The total sulfuric acid is not all obtained by this method, but it appears to have some advantages in the examination of peat for sulfur injurious to vegetation.

The sulfuric acid in a peat which is injurious to vegetation is classified by Fleischer, as follows:

(1) Free sulfuric acid, which is the excess obtained after calculation as sulfates of the bases in the water extract before combustion.

(2) The sulfuric acid contained as copperas, calculated from the ferrous oxid content of the aqueous extract.

(3) Sulfuric acid arising from the oxidation of pyrites calculated from the sulfuric acid obtained by combustion of the water-extracted sample. It will be noticed that no account is taken here of the sulfurous acid that might be due to organic sulfur in the peat.

A better idea of the distribution of the sulfur in the sample can be obtained by estimating it according to the method given in paragraph 429.

535. **Phosphoric Acid.**—A method for determining the phosphorus in peat is given in the next paragraph. The process given in 421 may also be used.

The method of extraction with hydrochloric acid is wholly unreliable as a means of determining the available phosphoric acid in peat.

There are some vegetable soils which contain so much iron and lime that the whole of the acid ordinarily used would be consumed thereby. In some cases it may be found useful to determine the quantity of phosphoric acid which can be extracted with dilute hydrochloric acid, and afterwards to separate the humus and determine the content of phosphoric acid therein.

536. **Estimation of Phosphoric Acid in Peat Soils.**—The amount of phosphoric acid obtained by extraction with hydrochloric or

sulfuric acid is markedly less in these soils than that obtained after the incineration of the sample, as pointed out by Schmöger.[95] This is due to the fact that the phosphoric acid is ordinarily combined in the form of nuclein. Extraction of the soils with ether shows that it is not present in the form of lecithin. The nuclein products, as is well known, are decomposed by heating in presence of acidified water at a high temperature for some time. The heating can either take place in an autoclave or in sealed glass tubes. The method is as follows:

The sample of soil is thoroughly rubbed up in a mortar with water, and then hydrochloric acid added until one gram of the water-free peat is suspended in about ten cubic centimeters of 12 per cent hydrochloric acid. The sample is placed in a glass or porcelain vessel in an autoclave and heated to 140°-160° for 12 hours. The phosphoric acid is determined in the extract in the usual way. The percentage of phosphoric acid determined in this way is found to correspond to the amount determined by the incineration of the substance.

The total phosphoric acid is determined in peats by the incineration of the sample and the estimation of the phosphoric acid in the ash. The phosphoric acid soluble in hydrochloric acid solution is determined by extracting a sample of the soil with 12 per cent hydrochloric acid in the usual way. The difference between this and the total is calculated as phosphoric acid in organic compounds.

Or the total phosphoric acid is determined by treating the soil with 12 per cent hydrochloric acid, in the proportion of one gram of soil to ten cubic centimeters of the acid, and the solution is placed in an autoclave and heated for ten hours to 140°-160°, as above described. The phosphoric acid is then determined by the usual method. The difference between the total phosphoric acid as thus determined and the phosphoric acid soluble in hydrochloric acid is calculated as phosphoric acid in organic compounds.

537. Humus.—The humus is estimated by the method of Huston and McBride, as given in paragraph **350**. In samples so rich

[95] Berichte der deutschen chemischen Gesellschaft, 1893, **26** : 386.

in organic matter as peat the method of Grandeau does not give good results.

Often more than half the weight of the dry substance is soluble in ammonia after treatment with acid. The nitrogen in the original sample and in the separated humus should be estimated by moist combustion with sulfuric acid in the usual manner.

538. The Mineral Contents of Humus.—The material obtained by precipitating the alkaline extract of a vegetable earth with an acid does not consist alone of oxygen, carbon, hydrogen, and nitrogen. The complex molecules which make up this mixture contain certain quantities of iron, sulfur, and phosphorus in an organic state. These bodies are left as inorganic compounds on ignition, provided there is enough of base present to combine with all the acid elements. Much of the sulfur and phosphorus, however, in these compounds might be lost by simple ignition. In such cases moist oxidation of these bodies must be practiced, or the gases of combustion passed over bodies capable of absorbing the oxidized materials in order to detect and determine them. The proper methods of accomplishing this have already been pointed out for vegetable soils, and the same processes are applicable in the case of extracted and precipitated humus.

Another proof that both phosphorus and sulfur are present in humus in an organic state is found in the fact pointed out by Eggertz and Nilson, that the ash of peat soils is always richer in sulfuric and phosphoric acids than the solution obtained therefrom by hydrochloric acid.[93]

In a sample of peat examined by them there was found in the ash 1.46 per cent SO_3, and in the acid extract only 0.05 per cent SO_3; and in the ash 0.3 per cent P_2O_5, while in the extract only 0.03 per cent P_2O_5.

539. Combustion of the Humus.—The percentage composition of the extracted humus can be determined, after drying to constant weight, by combustion with copper oxid. There is little use in trying to assign definite chemical formulas to any of the components of the complex which we call humus. Some of the sup-

[93] Biedermann's Central-Blatt für Agrikultur-Chemie, 1889, **18** : 664.

posed formulas which have been given (page 53) cannot, in the light of our present knowledge, be regarded as of any value.

540. Ether Extract.—Most peaty soils, when very dry, are not easily moistened with water. This is due to a superficial coating of fatty or resinous bodies which prevents the water from reaching the particles. In such cases water will pass between the particles and percolate to a considerable depth, but without wetting. This oily matter can be removed by treating the dry material with ether in any approved extraction apparatus. For the separation of the more purely fatty bodies, light petroleum may be used, while the total of such matters is extractable with sulfuric ether. The extracted bodies should be examined to determine their nature, whether fatty or composed of other materials soluble in ether. The quantity of this material in some peat soils is remarkably high. In a Florida peat, examined in the laboratory of the Bureau of Chemistry, 18.95 per cent of the air-dried substance, which contained still 41.83 per cent of water, or about 32.5 per cent of the water-free material were found to be soluble in ether.

The color of the ether extract may be almost black, showing the extraction of a part of the humus or coloring matter in the peat. This extractive coloring matter may also be a partial oxidation product of the original chlorophyl of the plant.

541. Further Examination of the Ether Extract.—The ether extract should be first treated with petroleum ether, unless this substance be used first in extraction. Afterwards, it is to be exhausted with strong alcohol, and the quantities of material soluble in the three reagents separately determined.

The nitrogen is further to be determined in the several extracts, and, for control, in the residue of the peat.

The method of procedure practiced in the laboratory of the Bureau of Chemistry is to first extract the sample with petroleum ether, which will yield any free fat acids, fats, or oils, waxes, and possibly some resinous matter. A weighed portion of the sample, about two grams, is extracted quantitatively by one of the methods which will be described in the second volume of this manual.

From two to five kilograms of the sample are then extracted

in bulk for the purpose of securing a sufficient quantity of the material to use for further analysis.[96]

In each case the petroleum is followed by sulfuric ether, and in this way the chlorophyl, resins, etc., are obtained. This extract is examined also for its several proximate contsituents.[97]

The treatment with ether is followed by extraction with absolute alcohol for the removal of tannins and other glucosides, resins insoluble in ether, etc., and the extract subjected to the usual examination. Instead of absolute alcohol a spirit of 95 per cent strength, or even of 80 per cent may be used. The final residue should be subjected to the usual determination for nitrogen, volatile matter, ash, etc., in the manner already described. The large amount of resinous and other matters soluble in petroleum and ether, which is found in the Florida peat soils, is probably due to the proximity of pine forests, the débris of which, sooner or later, find their way to these lacustrine deposits. Considerable portions of organic humic acids and even humus itself, may also be removed by ether and alcohol and in every case the nitrogen should be determined in these extracts.

542. Examination of the Acid Extract of Humus Soils.—Forster calls attention to the difficulties attending the analysis of the acid soluble constituents of soil.[98] Among these are mentioned the difficulty of washing out of the acid insoluble residue all dissolved material, particularly from clay or humus soils. The separation of the alkali earths and the alkalies from the voluminous iron and alumina precipitate is intricate and time consuming. Not less unsatisfactory is the separation of manganese by the usual methods.

As an improvement of the usual procedure, the author offers the following:

Solution in Ten Per Cent HCl.—From 100 to 200 grams of air-dry fine material are treated in a flask with ten per cent hydrochloric acid in the proportion of one gram of soil to two cubic centimeters of ten per cent acid. After removing carbon dioxid with a current of air, the flask and its contents are weighed and the mixture heated on the water-bath for three hours. After cooling,

[96] Dragendorff, Plant Analysis, London, 1884 : 8.

[97] Dragendorff, Plant Analysis, London, 1884 : 31.

[98] Chemiker Zeitung, 1894, **14** : 36-38.

the evaporated water is restored and the whole so diluted that for each gram of soil there shall be ten cubic centimeters of solution. Filter through a dry filter, evaporate from 800 to 1,600 cubic centimeters of the filtrate with from five to ten cubic centimeters of nitric acid to dryness; take up in hydrochloric acid and water and dilute so that each 100 cubic centimeters shall equal 40 or 50 grams of air-dry soil. This solution is used for the subsequent determination of potash, lime, magnesia, phosphoric acid and sulfuric acid.

Determination of Potash.—An aliquot part of the solution equal to from 20 to 50 grams of air-dry soil is evaporated to dryness in a platinum dish, ignited below redness and distilled water and a little hydrogen peroxid added to oxidize iron. To the hot solution add an excess of ammonium carbonate, filter, wash with hot water, and evaporate the filtrate to dryness, heat in air-bath one-half hour, then at 150°, and finally ignite below redness. Dissolve the residue in a little water, add sufficient barium chlorid solution and a drop of hydrochloric acid and again evaporate. Dissolve in water, and after filtering, determine potash with platinic chlorid as usual.

Determination of Phosphoric Acid.—An aliquot part of the solution equal to from 20 to 50 grams of air-dried soil is neutralized with ammonia, heated to 80° in a water-bath and 100 cubic centimeters of ammonium molybdate added and allowed to stand 15 minutes, and then filtered. Longer heating at lower temperatures is useless and to be avoided, as thereby molybdic acid in considerable quantity and iron are precipitated along with the ammonium phospho-molybdate and the ammonium magnesium phosphate thus contaminated. The precipitate is collected on a small filter that the wash solution and ammonia required for dissolving may be limited to the smallest required amount. The subsequent formation and complete separation of the ammonium magnesium phosphate precipitate is hastened by shaking from one-fourth to one-half hour.

Determination of Lime.—A part of the solution equal to 30 grams of soil (or less of a soil rich in lime) is made ammoniacal,

heated to boiling and a boiling solution of from four to five grams of ammonium oxalate is added and the whole heated to boiling again for a few minutes. After removing from the flame the solution is immediately made acid with acetic acid. If the solution is still brown in color, or if all the iron is not dissolved, add more ammonium oxalate and place the beaker in a boiling water-bath until the solution is clear and the iron is all dissolved. The precipitation of the calcium oxalate in ammoniacal solution before the formation of ferric oxalate is necessary because calcium oxalate is not completely precipitated in acetic acid in the presence of iron. The calcium oxalate, once formed, is insoluble. Filter on a double filter, wash with hot water, dry, burn the filter over a small flame and dissolve in hot dilute hydrochloric acid in a 150 cubic centimeter flask. Evaporate repeatedly with nitric acid to break up chlorids and precipitate with ammonium persulfate in nitric acid solution according to Marshall.[99] Add ammonium phosphate to combine with iron and alumina, make ammoniacal, and after cooling, add acetic acid in slight excess. Make up to volume, filter through a dry filter, and determine calcium as oxalate, as usual, in 100 cubic centimeters of filtrate.

Or, to the hydrochloric acid solution add sufficient ammonium phosphate, an excess of pure sodium hydroxid, and ammonium persulfate, and heat to boiling for three to five minutes, cool, make up to volume and filter through a folded filter and determine lime in 100 cubic centimeters of the filtrate in the usual manner.

The precipitation of manganese is not as complete with hydrogen peroxid as with ammonium persulfate. From an ammoniacal solution manganese phosphate is not precipitated, and therefore a fixed alkali is required, instead of ammonia. The presence of chlorids does not interfere with the precipitation from alkaline solutions. From acetic acid solution manganese phosphate is not precipitated. As the quantity of manganese is small both in soils and ashes, the error introduced by the co-precipitation of other metallic oxids (lime and magnesia) is negligible.

Determination of Magnesia.—To a part of the solution equal to 30 grams of air-dry soil add an excess of ammonium phosphate,

[99] Berichte der deutschen chemischen Gesellschaft, 1902, 35 : 3266.

and if a precipitate forms dissolve in hydrochloric acid. The solution must be clear and colorless as the brown precipitate produced by ammonia is difficultly soluble in ammonium citrate. Add sufficient ammonia to make the whole contain two per cent, shake for from one-fourth to one-half hour, add 50 cubic centimeters of ammonium citrate solution (as used for superphosphates) and shake again for from one-fourth to one-half hour. Precipitation from solutions in which the iron is completely dissolved in ammonium citrate or tartrate gives low results, but if precipitated as above the dissolved iron is without effect. The precipitate may be contaminated with lime, iron, aluminum and manganese. Filter, and wash with ammonia, dissolve in hydrochloric acid and wash filter with hot water. To the filtrate, add excess of ammonium oxalate, make ammoniacal, boil and add acetic acid. After shaking, separate the calcium oxalate by filtration and wash the filter thoroughly. To the filtrate add an excess of ammonium phosphate and sufficient ammonia to make the solution two per cent strength. Shake one-half hour, add 20 cubic centimeters of ammonium citrate and shake again for one-half hour. The precipitate still contains traces of iron, aluminum and manganese to remove which it is ignited in a platinum crucible, dissolved in hydrochloric acid and hot water. Add sufficient ammonium phosphate, then pure sodium hydroxid, oxidize with ammonium persulfate, heat to boiling, cool, add acetic acid in excess to make up to volume in a 150 cubic centimeter flask and in 100 cubic centimeters of the filtrate, determine magnesia in the usual manner.

The above scheme presents some novel or at least little practiced methods of procedure, but with the absence of comparative data there is little evidence of any superiority in the method, either for time-saving or accuracy over the methods in common use. It is offered more as a possible base for further investigation than as a process to be implicitly followed.

543. Acidity of Peat Soils.—The acid reaction of peaty soils, especially of the high peat soils, is aside from the presence of carbon dioxid, due to the presence of free humic acids or acid humates. An exact method for determining quantitatively the

acidity of the soil is not yet known, and especially is it desirable to have a method whereby the acidity of the peat soils can be determined with satisfactory exactness. It seemed worth while to make an attempt to determine the acidity of the peat soils by exhausting them with neutral solvents, such as salt solutions, etc., and estimating them for the acidity of the extract, in order to measure in some quantity the acidity in the substances which are present. These substances have very different degrees of solubility, and in addition to this the titration of extracts obtained in this way, inasmuch as they are colored by dissolved organic bodies, is either impossible or extremely difficult. Some of these coloring matters themselves possess the quality of an indicator, and in such cases the titration is more easily accomplished. There is, moreover, a radical objection to the use of bases in the titration of acid extracts from peaty soils. Since humus bodies which are present and which are not of an acid nature, under the influence of bases and the presence of oxygen are decomposed with the formation of humus acids, this decomposition in the presence of basic bodies and oxygen takes place often with great rapidity. The faculty is ascribed to humus acids of displacing carbon dioxid from carbonates. Whether this capacity is possessed by all the humus acids, or only by some of them, is not known. Humic acids of this kind, however, must be placed in the first line of those which cause the acidity of peat soils, and to these acids are doubtless due the vigorous chemical and physiological phenomena which humus acids in general produce.

Tacke proposes to determine the total acidity of peat soils by the method which is described in paragraph **357**.

The carbonate which is to be used for decomposition under the influence of the acid humates must be a neutral reacting body, so that if it is in the cold it can exert no decomposing influence upon the humus substances. The presence of oxygen, through the influence of which the decomposition of the humus substance may take place with the formation of carbon dioxid, is to be prevented, therefore the humus acids must work upon the carbonate in an atmosphere free of oxygen, or in a vacuum. On account of the difficult solubility of certain humic acids the substance must

be in its finest possible state of subdivision. The carbonate also must be in a similarly fine state of division, which is best secured by obtaining the silt through action of water, or the carbonate of lime may be used in the form of freshly precipitated lime carbonate.

RARE CONSTITUENTS OF SOILS.

544. Estimation of Copper.—The natural occurrence of copper in many vegetables has acquired additional significance by reason of its relation to the copper which may find its way into cultivated soil from the large quantities of copper compounds used as fungicides. Copper cannot be regarded, in any sense, as a plant food. It can only be considered as an accidental and non-essential constituent of vegetable matter. It is by no means certain, however, that copper may not be, in some sense, in organic combination, as phosphorus and sulfur often are. It is said to be found in certain animal organisms, notably in the oyster. In the estimation of soluble copper in soils, there is first made a hydrochloric acid solution of the sample. The solution is treated with well-washed hydrogen sulfid until saturated. The precipitate is collected at once on a gooch, washed with water containing the precipitating reagent, dried, gently ignited or roasted, and dissolved in aqua regia. After evaporating to dryness on a steam-bath, water and hydrochloric acid are added, and the copper re-precipitated in the manner described above.

If zinc be present in the sample the solution should be made very strongly acid with hydrochloric before the treatment with hydrogen sulfid, otherwise some zinc may be carried down with the copper.[1] If lead be present it is also precipitated with the copper and can be separated as described below. The precipitate is treated as above and in the filtrate from the solution in nitric acid after the second precipitation the copper is precipitated as hydroxid by potash, collected in a porcelain gooch, dried, ignited, and weighed as CuO. Or the copper may be secured as sulfate and estimated electrolytically in the manner described in volume third for the gravimetric estimation of sugar. In very minute

[1] Journal für praktische Chemie, 1858, **73** : 241.

quantities copper may also be determined colorimetrically as follows:

The previous separation of the copper by the process described above is often unnecessary and the determination may be accomplished directly as follows:

Evaporate the soil solution containing the copper to dryness and digest on the steam-bath for one-half hour with nitric acid, evaporate to dryness with the addition of one cubic centimeter of concentrated sulfuric acid and heat until white fumes are given off. Digest on the steam-bath with 25 centimeters of water and a few drops of nitric acid, filter and precipitate the copper by electrolysis. Dissolve the copper from the electrode with nitric acid and evaporate. Dissolve in water with the addition of one drop of nitric acid. If there is sufficient copper present it is estimated gravimetrically or by titration. If there are only a few tenths of a milligram it is determined by the colorimetric method which is as follows: In a large nessler cylinder place five drops of potassium ferro-cyanid, add the copper solution and five cubic centimeters of ammonium nitrate. The color is then compared with a cylinder filled in the same way with a solution containing a known amount of copper.

545. **Estimation of Lead.**—If the soil contain lead this metal will be thrown down with the copper as sulfid in the manner described above. In this case the mixed sulfids are dissolved in nitric acid, diluted with water, filtered, and the filter well washed. The filtrate is treated with sulfuric acid in considerable excess, and evaporated until all the nitric acid has passed off and the sulfuric acid begins to escape. After cooling, water is added and the lead sulfate collected on a porcelain gooch and washed with water containing sulfuric acid. Finally it is washed with alcohol, dried, ignited, and the lead weighed as $PbSO_4$.

546. **Estimation of Zinc.**—If zinc be present in the hydrochloric acid extract of a soil it may be estimated as carbonate after freeing it carefully of iron. The principal part of the iron should first be separated in the usual way by sodium acetate. In the warm solution (acid with acetic) the zinc is precipitated by hydrogen sulfid in excess. The beaker in which the precipitation

takes place should be left covered in a warm place at least 12 hours. After collecting the zinc sulfid on a filter it is washed with water saturated with hydrogen sulfid. In order to free the zinc from every trace of iron it is better to dissolve the precipitate in hot dilute hydrochloric acid and reprecipitate as above, and, after boiling with some potassium chlorate, saturate it with ammonia. Any remaining trace of iron is precipitated as ferric hydroxid while the zinc remains in solution. The ferric hydroxid is separated by filtration and the filtrate, after acidifying with acetic, is treated with hydrogen sulfid as above. The zinc sulfid is dissolved again in hot hydrochloric acid, oxidized with potassium chlorate, the acid almost neutralized with soda and the zinc precipitated as carbonate with the sodium salt. After precipitation, the contents of the beaker are boiled until all free carbon dioxid is expelled, the carbonate collected on a filter, washed with hot water, dried, ignited, and weighed as ZnO.

547. **The Occurrence of Strontium in Soils.**—Strontium, though chemically associated with calcium by reason of their class and reaction similarities, is not generally recognized as a constituent of the ash of plants, and therefore is not regarded as a soil constituent. Its occurrence in certain barks has been pointed out by Trimble.[2] The barks examined were chiefly of the genus Castanopsis and two oaks from Singapore. The ash of these samples yielded notable quantities of strontium. Whether strontium can replace lime in any of the functions of plant growth has not been determined. Its presence appears more likely to be due to local causes.

When strontium is found in the ash of plants, it may be separated from calcium in the course of analysis by the usual process.

The strontium is precipitated with the calcium as oxalate. The precipitate is ignited, dissolved in hydrochloric acid, boiled with ammonia to separate any traces of iron or alumina, and after filtering reprecipitated with ammonium oxalate. The precipitate is ignited, finally over the blast until the oxids are formed, dissolved in nitric acid, evaporated to dryness and heated to 150° and the nitrates separated either by ether-alcohol,[3] or by amyl-alcohol.[4]

[2] American Journal of Pharmacy, 1897, **69** : 296.
[3] Zeitschrift für analytische Chemie, 1893, **32** : 189 and 312.
[4] American Journal of Science, 1892, [3], **16** : 50 and 314.

548. Boric Acid.—Boron, while not regarded as an essential plant food, is found quite uniformly in the ashes of a large number of plants. It may, therefore, be of some interest to the agricultural analyst to determine if any of its compounds be present in a soil extract or mineral water. For this purpose the following method may be employed. To one liter of the water or soil solu-

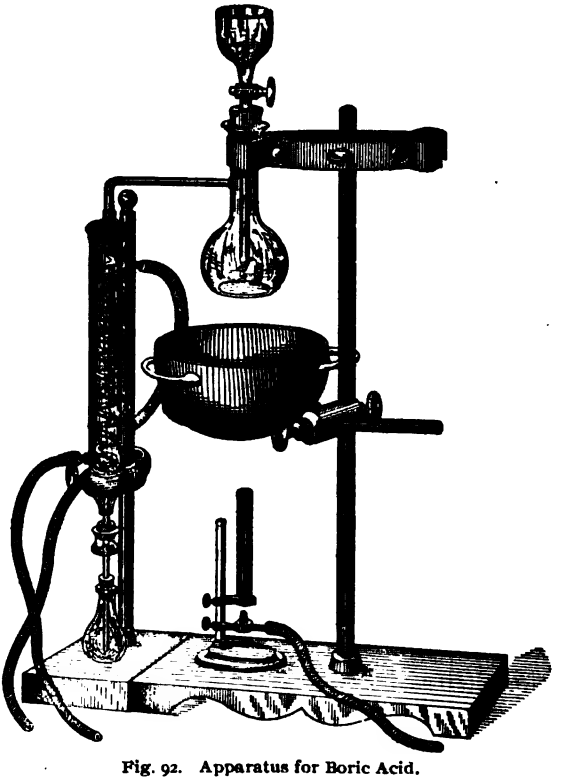

Fig. 92. Apparatus for Boric Acid.

tion supposed to contain boric acid add enough sodium carbonate to produce distinct alkalinity. After evaporation to dryness acidify the residue with hydrochloric acid, apply a piece of turmeric paper and dry at a moderate heat. The development of a brown-red tint will reveal the presence of boric acid.

The qualitative method suggested by Howard[5] for the detection of minute quantities of turmeric in mustard has been employed by

[5] Science, 1904, **19** : 583.

Bigelow and Brinton under carefully controlled conditions for the quantitative estimation of boric acid in minute quantities. This method may be applied to a soil solution as follows.

One or two liters of the solution are made slightly alkaline by means of lime water, evaporated to dryness and ignited. The residue is then dissolved in a small amount of water, the solution diluted to a convenient volume, and an aliquot portion, about ten cubic centimeters transferred to a platinum dish, and treated with one cubic centimeter of concentrated hydrochloric acid.

A strip of turmeric paper 15 millimeters wide and 250 millimeters long, prepared by dipping strips of porous filter paper into a solution of 50 cubic centimeters of curcumin in 100 cubic centimeters of alcohol, and drying, is then suspended with the lower end dipping into the top of the solution. The boric acid is carried up by capillarity and concentrated in a zone just below the highest point at which the paper is wet by the solution.

The maximum color is obtained by this method in about four hours, and is compared with solutions containing known amounts of boric acid and treated in the same manner. This method, as applied by Bigelow and Brinton to solutions of boric acid varying from one part in 100,000 to one part in 1,000,000, determines these minute quantities with a fair degree of precision.

Only bohemian glassware should be used in preparing the solutions since other varieties often contain boron as a constituent.

The quantitative estimation of the acid when present in notable quantity is accomplished as follows:[6] One or more liters of the water or soil solution rendered alkaline by sodium hydroxid and then acidified by nitric or acetic acid are evaporated to dryness in the distillation flask, shown in Fig. 92. About one gram of recently ignited pure lime, cooled in a desiccator and weighed accurately, is introduced into the receiving flask at the bottom of the condenser and slaked by a few cubic centimeters of water. When the flask is attached, the terminal tube of the condensing apparatus should dip into the lime-water in the receiving flask. The heating-bath is partly filled with paraffin at a temperature of about 120°. After cooling somewhat, ten cubic centimeters of methyl-alcohol are introduced into the distillation flask by means

[6] Gooch: American Chemical Journal, 1887, 9 : 23.

of the stoppered funnel-tube. The paraffin-bath is raised so that the entire bulb of the flask is immersed therein and the distillation continued until all the liquid has been distilled. This operation with methyl-alcohol is repeated five times. The boric acid passes off with the distillate and is found in the flask below the condenser as calcium borate. The contents of the distillation flask are evaporated to dryness and ignited conveniently in the same crucible in which the lime was burned. The increase in weight represents the quantity of boric anhydrid, B_2O_3, obtained.

549. **Method of Moissan.**—The principle of the method of Gooch which has just been described, is applied by Moissan in a slightly modified manner.[1]

In this method the generating flask is made smaller than in the gooch apparatus, and the funnel at the top is oval and provided with a ground-glass stopper. It is closed at the bottom with a glass stop-cock, and the slender funnel-tube enters through a rubber stopper and ends about the middle of the bulb of the flask. The delivery-tube connecting the distilling flask with the condenser is longer than in Fig. 91, and is bent upward at its middle part in the form of an obtuse angle. The receiving flask is connected with the condenser by means of a tube-shaped funnel, which prevents any regurgitation into the generating flask. The receiving flask also has attached to it a three-bulb potash absorption tube, through which all vapors escaping from the receiving flask must pass. The bulbs contain a five per cent solution of ammonia. The receiving flask should be placed in a crystallizing dish and kept surrounded with ice-water.

The boron which is to be estimated should be in the form of boric acid. This can readily be secured by treating the residue to be analyzed with nitric acid in a sealed tube. The mixture is introduced into the generating flask, washing with a little nitric acid, and evaporated to dryness. The heat is removed, and, by means of the funnel, ten cubic centimeters of methyl-alcohol added, and the distillation is renewed. This operation with methyl-alcohol is repeated four times, taking care to distill to dryness in each caes before the addition of a fresh quantity of alcohol. After-

[1] Bulletin de la Société Chimique de Paris, 1894, [3], 11 : 955.

wards, there is introduced into the apparatus one cubic centimeter each of distilled water and nitric acid and the distillation again carried to dryness. The treatment with methyl-alcohol, as described above, is then repeated three times. To determine whether all the boric acid has passed over, the receiving flask at the bottom of the condenser is disconnected and a drop of the alcohol taken from the end of the condensing tube by means of a filament of filter paper. On burning, the flame should not show any trace of green. In case a green color is observed, the distillation with nitric acid and methyl-alcohol must be repeated.

The ammonia in the potash bulbs serves to arrest any of the vapors carrying boric acid which might escape from the receiving flask. The contents of the bulbs are to be mixed with the liquid in the receiving dish, and the whole poured onto a known weight of recently ignited calcium oxid contained in a platinum dish, and the mixture briskly stirred. If the liquid be very acid the platinum dish should be kept in ice-water to prevent heating. After 15 minutes the liquid usually becomes alkaline, and it is then evaporated at a temperature below the boiling-point of methyl-alcohol (66°). The mass, after the methyl-alcohol has disappeared, is dried at a gradually increasing temperature, and finally, the dish is ignited over a blast, at first covered and afterwards open. This dish is covered and weighed and again ignited until constant weight is obtained.

The lime used should be specially prepared by igniting calcium nitrate incompletely, and reigniting a portion of this to constant weight just before beginning each analysis. The calcium oxid is then obtained in a perfectly fresh state. It should be employed in considerable excess, for each half gram of boric acid at least eight grams of the lime. The operation is tedious but the results are quite accurate.

550. Volumetric Estimation of Boron.—The gravimetric determinations, described above, are time consuming and successful efforts have been made to substitute volumetric processes therefore. The best of these methods is based on the process described by Jones,[8] which depends on the titration of the boric acid in

[8] American Journal of Science, 1899, [4], 7 : 147.

presence of a carbohydrate. A clearer acid reaction is thus manifested which renders the indicator more accurate and satisfactory.

Glycerol has the same effect and is the best material for sharp reactions, except for the impurities it may contain. For general purposes mannite is to be preferred.

The method of procedure is that described in Sutton's Volumetric Analysis.[9] The soil solution containing boric acid after the removal of the phosphoric acid is evaporated to dryness after being made alkaline, ignited to destroy organic matter, the ash dissolved in dilute acid, again rendered alkaline, filtered, and the boric acid determined in the filtrate after neutralization and the addition of mannite. None of the methods given above, except the turmeric paper process, is of value unless the quantity of boric acid amounts to at least one-tenth of one per cent, which is rarely the case with soils.

551. Occurrence and Determination of Titanium in Soils.—The disturbing effects of the presence of titanium in the analysis of soils has not been noticed by agricultural chemists until recently. West has called attention to the presence of titanium in the ashes of many plants and infers that it is an element very commonly absorbed by growing vegetation.[10] It is found in the ash of oak and apple wood, in apples, cow peas and cottonseed meal. It is also found in bituminous and in large quantities in anthracite coal. The wide distribution of titanium in the soil is not surprising when its common occurrence in minerals and rocks is taken into consideration.[11] The titanium, which is of interest to the soil analyst, is that found in solution with the iron and alumina.

On account of the great insolubility of titanium phosphate some care is required to separate the titanium when iron, alumina and phosphoric acid are found in hydrochloric acid solution of the soil.

To separate the titanium the modified method of Baskerville, as described by Bain may be used.[12] The acid is neutralized by ammonia and saturated with sulfurous acid and boiled for three

[9] Sutton's Volumetric Analysis, 1904, 9th edition, 94.

[10] Journal of the American Chemical Society, 1896, **18** : 403.

[11] Clarke and Hillebrand, Bulletin No. 148, United States Geological Survey, Washington, 1897, 65 et seq.

[12] Journal of the American Chemical Society, 1903, **25** : 1081.

minutes to precipitate the titanium dioxid. The precipitate is dissolved in hydrochloric acid 1:1. Any flocks of titanium phosphate which resist solution are digested with the hot acid until finally dissolved. The solution is again neutralized with ammonia and the titanium dioxid again precipitated by sulfurous acid. If not pure white the precipitate is collected and fused with sodium carbonate and the melt dissolved in sulfuric acid. Any insoluble residue is subjected to the same treatment as above, and the whole solution, after suitable dilution, treated with ammonia in excess. The precipitate is collected, dissolved in hydrochloric acid, neutralized with ammonia and precipitated with sulfurous acid. The titanium dioxid is collected, dried, ignited, and weighed. The substance as thus prepared still contains a trace of iron. For a more detailed description of the approved methods of separating and determining titanium Bain's article cited above may be consulted. The colorimetric method of determining titanium is described in paragraph 436.

552. **Method of Pellet and Fribourg.**—Pellet and Fribourg have studied very carefully the influence of titanium upon the determination of alumina in the presence of oxid of iron and of phosphoric acid and have suggested some slight modifications in the methods of preparing the soil solutions for determination.[13]

The investigations which have been made refer also to the determination of titanium in the ashes of vegetable substances in quantities where the amount is less than .2 of one per cent. In the preparation of the solution for analysis 30 grams of hydrofluoric acid are placed in a platinum capsule and in small quantities there is added a quantity of about three grams of dry, finely pulverized soil, and finally three cubic centimeters of pure sulfuric acid, and the mixture evaporated on a sand bath. The residue is lightly ignited just to reach complete dryness but not sufficient to decompose the sulfates which are formed. The mass is coarsely pulverized with a spatula and mixed with 15 grams of bisulfate of potassium and fused.

After cooling, the mass is detached from the platinum dish and coarsely pulverized, dissolved in from 200 to 250 cubic centimeters of water at a temperature of 60 degrees, cooled, the volume completed to 300 cubic centimeters, filtered, in order to

[13] Annales de Chimie analytique, 1905, **10** : 413.

separate any traces of sand, and 250 cubic centimeters of the filtrate, that is, an amount corresponding to 2.5 grams of the soil, are placed in a flask of 400 cubic centimeters capacity.

Forty cubic centimeters of the residue of the filtrate are titrated with a solution of potassium hydroxid of a strength sufficient for ten cubic centimeters thereof to neutralize five grams of potassium bisulfate. To the 250 cubic centimeters of the filtrate there is then added a quantity of potassium hydroxid sufficient to neutralize all the potassium bisulfate therein, except five grams. There is finally added a solution of sulfurous acid of 1020 to 1025 density freshly prepared, the solution boiled for two hours, and during the boiling there are twice added 50 cubic centimeters of the sulfurous acid solution.

The contents of the flask are then put upon a filter and washed with boiling water, dried and burned. This precipitate is almost pure titanic acid, containing only a little phosphoric acid. It is remelted with two grams of carbonate of potash, taken up with boiling water and filtered, and washed with a two per cent solution of carbonate of potash. The titanic acid then remains in the form of insoluble titanate. A very small portion passes into solution and this error is corrected by determinations with known quantities of pure titanic acid. The insoluble titanate is burned, afterwards melted with one gram of bisulfate of potassium and reprecipitated, as described above. The TiO_2 obtained is ignited and the quantity obtained is added to that found by fusion with the carbonate of potash.

In the estimation by the colorimetric method, half a gram of soil or 2.5 grams of ash are treated with hydrofluoric acid, as described above. The residue is detached from the platinum capsule, which is easily accomplished, pulverized with a spatula and mixed with five grams of bisulfate of potash, fused, taken up in distilled water containing 15 per cent of pure sulfuric acid at a maximum temperature of 60 degrees, cooled, and the volume completed to 100 cubic centimeters. Of this quantity from one to ten cubic centimeters, according to the content of titanium, are made up to ten cubic centimeters with distilled water, and five cubic centimeters of hydrogen peroxid added, and the color produced compared in a colorimeter with a solution prepared with a pure solution of titanic acid containing from one-tenth to one gram of the acid per liter.

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